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U.S. Army Environmental Center

TREATABILITY STUDY REPORT FOR REMEDIATION OF CHEMICAL WARFARE AGENT CONTAMINATED SOILS USING PEROXYSULFATE EX-SITU TREATMENT

Prepared for
U.S. ARMY ENVIRONMENTAL CENTER
Aberdeen Proving Ground, Maryland 21010-5401

Prepared by
Tennessee Valley Authority
Environmental Research Center
Muscle Shoals, Alabama 35662-1010

July 1996

TVA Contract No. TV-99704V
Report No. SFIM-AEC-ET-CR-96181

Treatability Study Report
for
Remediation of Chemical Warfare Agent Contaminated Soils
Using Peroxysulfate Ex-Situ Treatment

Prepared for

U.S. Army Environmental Center
Environmental Technology Division
Aberdeen Proving Ground, MD 21010-5401
POC: Mr. Louis Kanaras

Prepared by

J. Richard Pugh
John H. Grinstead
James A. Farley
Paul D. Enlow
and David A. Kelly
of the
Tennessee Valley Authority
Environmental Research Center
Muscle Shoals, AL 35662-1010

AND

Louis Kanaras
of the
U.S. Army Environmental Center
Environmental Technology Division
Aberdeen Proving Ground, MD 21010-5401

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TVA Contract No. TV-99704V

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

Form Approved OMB No. 0704-0188

1a. REPORT SECURITY CLASSIFICATION: Unclassified	1b. RESTRICTIVE MARKINGS
2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT: Unlimited
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE	
4. PERFORMING ORGANIZATION REPORT NUMBER(S)	5. MONITORING ORGANIZATION REPORT NUMBER(S): SFIM-AEC-ET-96181
6a. NAME OF PERFORMING ORGANIZATION: Tennessee Valley Authority / 6b. OFFICE SYMBOL (If applicable): CEB 4C-M	7a. NAME OF MONITORING ORGANIZATION: U.S. Army Environmental Center
6c. ADDRESS (City, State, and ZIP Code): TVA Reservation, Post Office Box 1010, Muscle Shoals, Alabama 35662-1010	7b. ADDRESS (City, State, and ZIP Code): Aberdeen Proving Ground, Maryland 21010-5401
8a. NAME OF FUNDING/SPONSORING ORGANIZATION: U.S. Army Environmental Center / 8b. OFFICE SYMBOL (If applicable): SFIM-AEC-ET	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER: MIPR 4456, TVA Contract No. TV-99704V
8c. ADDRESS (City, State, and ZIP Code)	10. SOURCE OF FUNDING NUMBERS: PROGRAM ELEMENT NO. / PROJECT NO. / TASK NO. / WORK UNIT ACCESSION NO.

11. TITLE (Include Security Classification)
Treatability Study Report for Remediation of Chemical Warfare Agent Contaminated Soils Using Peroxysulfate Ex-Situ Treatment.

12. PERSONAL AUTHOR(S)
J.R. Pugh; J.H. Grinstead, Jr.; J.A. Farley; P.D. Enlow; D.A. Kelly; & Louis Kanaras

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Final	FROM _____ TO _____	1996, July	

16. SUPPLEMENTARY NOTATION

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	Remediation of Chemical Warfare Agent Contaminated Soils Using Peroxysulfates.

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

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20. DISTRIBUTION/AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION	
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS	Unclassified	
22a. NAME OF RESPONSIBLE INDIVIDUAL: Louis Kanaras	22b. TELEPHONE (Include Area Code): (410) 612-6854	22c. OFFICE SYMBOL: SFIM-AEC-ET

DD Form 1473, JUN 86 — Previous editions are obsolete. — SECURITY CLASSIFICATION OF THIS PAGE

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ABBREVIATIONS

CEES	Chloroethyl ethylsulfide; $ClH_2CH_2SCH_2CH_3$
CEPSI	Chloroethyl phenylsulfide; $C_6H_5SCH_2CH_2Cl$
CEPSO	Chloroethyl phenylsulfone; $C_6H_5(CH_2CH_2Cl)SO_2$
CEPSX	Chloroethyl phenylsulfoxide; $C_6H_5S(O)CH_2CH_2Cl$
CWA	Chemical warfare agent
CWM	Chemical warfare material
DIMP	Diisopropyl methylphosphonate; $CH_3PO(OCH(CH_3)_2)_2$
DMMP	Dimethyl methylphosphonate; $CH_3PO(OCH_3)_2$
DoD	Department of Defense
GB	Isopropyl methylphosphonofluoridate; $CH_3P(O)F(OCH(CH_3)_2$
GC	Gas Chromatography
GC/MS	Gas Chromatography / Mass Spectrometry
H_2O_2	Hydrogen peroxide
HD	Bis(chloroethyl)sulfide; $S(CH_2CH_2Cl)_2$
HEES	Hydroxyethyl ethylsulfide; $CH_3CH_2SCH_2CH_2OH$
HEPSI	Hydroxyethyl phenylsulfide; $C_6H_5SCH_2CH_2OH$
HEPSO	Hydroxyethyl phenylsulfone; $C_6H_5(CH_2CH_2OH)SO_2$
HEPSX	Hydroxyethyl phenylsulfoxide; $C_6H_5S(O)CH_2CH_2OH$
HPLC	High Performance Liquid Chromatography
HSO_5^-	Peroxymonosulfate ion
IC	Ion Chromatography
mM	milliMolar, 1×10^{-3} moles per liter of solution.
MΩ	megaohm
Mp	Melting Point
MPA	Methylphosphonic acid; $CH_3PO(OH)_2$
NHE	Normal Hydrogen Electrode
O_3	Ozone
OSDEPPT	O-ethyl S-ethyl phenylphosphonothioate
PVSO	Phenyl vinylsulfone; $C_6H_5(CHCH_2)SO_2$
$S_2O_8^{2-}$	Peroxydisulfate anion
$SO_4^{\cdot-}$	Sulfate radical anion
TDG	Thiodiglycol; $S(CH_2CH_2OH)_2$
TiO_2	Titanium dioxide
TVA	Tennessee Valley Authority
TVA RM	Tennessee Valley Authority Resource Management
USDA	United States Department of Agriculture
USAEC	United States Army Environmental Center
V	Volt
VX	O-ethyl-S-2-(diisopropylamino)ethyl methylphosphonothiolate; $CH_3P(O)(OCH_3CH_2)SCH_2CH_2N(CH(CH_3)_2)_2$

EXECUTIVE SUMMARY

This project was initiated to determine the feasibility of using peroxysulfate based oxidants to remediate soils contaminated with GB, HD, and VX. Prior research indicated that peroxydisulfate rapidly mineralizes VX, HD, and GB in aqueous solutions at moderately elevated temperatures (66-90 °C). But it was unclear whether mineralization would occur in soil-bearing slurries. This project was designed to determine whether soil-borne chemical warfare agent simulants would in fact degrade when exposed to slurries containing the oxidants. In particular the project was to determine:

- Whether the oxidants have substantial selectivity for the target compounds or be consumed by soil or other non-target materials.
- The rate of simulant degradation.
- When possible, whether the simulants were mineralized and if not, then what degradation products were formed.

The study results indicate that, at temperatures ranging between 75 and 90 °C, peroxysulfates will degrade between 99.999 to 99.99999 percent of the exposed simulants within three hours. Evidence of nearly complete mineralization of the HD and VX simulants was observed when peroxydisulfate was used. However, the GB simulant's reaction intermediates were not completely mineralized and the VX simulant's reaction intermediate took about ten hours to degrade. The ability to rid contaminated soils of organic byproducts make peroxydisulfate a promising compound for soil remediation.

The behavior of specific chemical warfare agent simulants upon exposure to peroxysulfate oxidants are as follows:

- At 75 °C peroxydisulfate degraded slurries containing the HD simulants to below the detection limit within 3 hours. Sulfone oxidation by-products were similarly

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- Based on the laboratory results, a conceptual design for a small batch demonstration plant capable of processing up to 750 pounds (340 Kg) of contaminated soil per shift was developed. The cost for constructing this unit has been estimated at $450,000. The plant is designed to be transportable and could be used both as a demonstration plant and as a post demonstration treatment facility.

Due to the promising results listed above, TVA RM recommends that work on the peroxysulfate process be continued as a potential demonstration program. This program is envisioned to be executed in five phases as follows:

- Phase I - A laboratory study in which chemical warfare agents (HD, GB, and VX) would be used to verify the results of the current study, confirm agent mineralization, and to develop a better understanding of the underlying chemistry.

- Phase II - A laboratory study focused on the collection of process design and Health and Safety related information.

- Phase III - Design of a demonstration facility.

- Phase IV - Construction of a demonstration facility.

- Phase V - Demonstration of the technology.

Use of the five phase approach will allow periodic review of project progress between phases and provides opportunities to periodically reassess project viability as the program progresses.

SECTION 1

INTRODUCTION

1.1 General Background

There are 227 identified sites at 93 locations across the United States where nonstockpile Chemical Warfare Materials (CWM) have been buried or discharged. Additional sites are still being identified.[1] These materials include both contained materials (mortar rounds, bombs, drums, etc.) and discharged material. In addition, CWM have migrated into ground water at some of the sites.[2] Until recently, the Department of Defense (DoD) was emphasizing the cleanup of stockpiled materials, so limited emphasis was placed on nonstockpiled materials or contaminated soils. In part, this occurred because laboratory results predicted rapid degradation rates for chemical warfare agents exposed to the environment. However, several incidences have been reported where CWM was uncovered in soil decades after burial.[3]

As part of the DoD's program to combat soil contamination, the U.S. Army Environmental Center (USAEC) contracted with Tennessee Valley Authority Resource Management (TVA RM) to investigate the feasibility of using peroxysulfate based oxidants as a means of remediating soils contaminated with GB, HD, and VX. The TVA RM work is being conducted with chemical agent simulants.

Peroxysulfate compounds have been investigated for decontaminating the surface of chemical warfare agent (CWA) contaminated materials.[4] However, this work focused on the rapid decontamination of battlefields, laboratories, production plants, and destruction sites rather than on soil decontamination. Because soil remediation was not a priority, the application of peroxysulfate compounds to the remediation of soil contaminated with chemical warfare agents has not been investigated up to this point.

The physical and chemical characteristics of peroxysulfate compounds make them attractive for use in soil remediation. Peroxydisulfate completely mineralize chemical warfare agents, including GB[5] so lengthy bioremediation post treatments are not necessary -- unlike the situation when hydrolysis or nucleophilic techniques are employed. In addition, both peroxymonosulfate and peroxydisulfate react rapidly with chemical warfare agents such as HD[6] and VX[7], are water soluble, do not require light or metal catalyzed activation, and are more stable in soils than comparable oxidants.[8]

This report summarizes TVA RM's findings for HD, GB and VX simulants and provides a conceptual design/cost estimate for a demonstration-scale remediation system. The simulants used were:

- Chloroethyl ethylsulfide (CEES) and chloroethyl phenylsulfide (CEPSI) for mustard (HD)
- Diisopropyl methylphosphonate (DIMP) for GB.
- O-ethyl S-ethyl phenylphosphonothioate (OSDEPPT) for VX.

This study also introduces the use of Raman spectroscopy as an alternative to traditional titration methods for tracking peroxysulfate concentrations in solution. The use of Raman spectroscopy is a critical component of this study because optimization of process conditions requires knowledge of the reactivates of the various oxidants at specific conditions. Titration determines only the total amount of oxidant in solution and does not differentiate between peroxydisulfate, peroxymonosulfate, and hydrogen peroxide.

Previous research indicates that differentiation between the peroxysulfate species is important because, for example, peroxydisulfate mineralizes VX while peroxymonosulfate cannot and hydrogen peroxide may not react at all. Previous attempts to degrade VX with peroxydisulfate solutions found that, at high pH, the rate was limited

by low VX solubility and rapid peroxydisulfate decomposition.[7] At low pH, the VX was rapidly degraded, but not mineralized.

The results above fit well with the known chemistry of peroxysulfate compounds. In solution, peroxymonosulfate and peroxydisulfate establish a complex equilibrium as they degrade to sulfate and hydrogen peroxide. At high pH, peroxydisulfate reacts with water to produce sulfate and O_2. At low pH, the peroxydisulfate degrades to peroxymonosulfate then further to hydrogen peroxide and sulfate.

Raman spectroscopy works by detecting the O-O and S=O stretching vibrations for HSO_5^- and $S_2O_8^{2-}$, the O-O stretch for H_2O_2, and the S=O stretch for SO_4^{2-}. Unlike infrared spectroscopy, water does not interfere with the Raman-active vibrations. The Raman-active stretching frequencies for each are resolvable and enable the detection of each species. Raman follows the scattering equivalent of Beer's law, so the area under the detected peaks can be used to quantify the amount of each species in solution. The technique is nondestructive and noninvasive, and is ideal for integration into a process stream as well as for use in laboratory analysis.

1.2 Description of Peroxysulfate Technology

1.2.1 Applications

Previous research conducted by TVA RM demonstrated that peroxysulfate aqueous solutions are highly effective at remediating hydrocarbon contaminated soils. Peroxysulfate compounds are more stable in soil than comparable strong oxidants. In addition, peroxysulfates readily oxide organic molecules and have long been associated with the degradation of chemical warfare agents.

Peroxysulfates have been shown to rapidly degrade many chemical warfare agents and simulants in aqueous solutions.[4] Peroxymonosulfate degrades HD to sulfone oxidation

products[6] and VX to ethyl methylphosphonic acid and a sulfonic acid.[7] However, peroxymonosulfate does not oxidize GB unless catalyzed.[9] Peroxydisulfate completely mineralizes HD[10] and VX,[11] as well as GB simulants such as DIMP and DMMP.[5]

1.2.2 Description

TVA believes that chemical warfare agent-contaminated soils may be remediated by slurrying the soils in an aqueous peroxysulfate solution. Peroxysulfate appears particularly promising because the sulfate radical anions produced within an aqueous peroxydisulfate solution are able to oxidize virtually any organic molecule. Similar technology has been used in total organic carbon monitors.[12] Sulfate radical anions can be generated one of two ways:

- By heating peroxydisulfate (equation 1)

$$S_2O_8^{2-} + \Delta \rightarrow 2\ SO_4^{\cdot -} \qquad (1)$$

- By light- or reduction-induced generation of peroxydisulfate or peroxymonosulfate (equations 2 and 3).[7]

$$S_2O_8^{2-} + Ag^+ \rightarrow SO_4^{\cdot -} + SO_4^{2-} + Ag^{2+} \qquad (2)$$

$$HSO_5^- + Ag^+ \rightarrow SO_4^{\cdot -} + OH^- + Ag^{2+} \qquad (3)$$

Once generated, $SO_4^{\cdot -}$ rapidly oxidizes chemical warfare agents. This is shown for the oxidation of HD to CO_2, SO_4^{2-}, and Cl^-, in equation 4.

$$12\ SO_4^{\cdot -} + (ClCH_2CH_2)_2S + 12\ H_2O \rightarrow 4\ CO_2 + 2\ Cl^- + 13\ SO_4^{2-} + 32\ H^+ \qquad (4)$$

In addition, peroxysulfate compounds directly oxidize the chemical warfare agents, at room temperature, via the reactions shown in equations 5 and 6. The sulfone product of these reactions is not readily degraded further unless sulfate radical anions are involved, as in equation 4.

$$HSO_5^- + (ClCH_2CH_2)_2S \rightarrow HSO_4^- + (ClCH_2CH_2)_2S{=}O \qquad (5)$$

$$HSO_5^- + (ClCH_2CH_2)_2S{=}O \rightarrow HSO_4^- + (ClCH_2CH_2)_2SO_2 \qquad (6)$$

1.2.3 Advantages and Limitations

The primary advantage of using peroxysulfates, and peroxydisulfate in particular, is that they can mineralize chemical warfare agents. The only remaining products are relatively innocuous salts such as Cl^-, PO_4^{3-}, and SO_4^{2-}. Presumably, after pH adjustments and careful characterization of the treated soils, landfilling will not be required.

Use of peroxysulfate methods have other advantages as well. When VX and HD are remediated by hydrolysis methods, the rate of VX hydrolysis is limited by slow dissolution under the basic conditions required. In contrast, Oxone solutions are acidic, and peroxydisulfate solutions can be made acidic, so peroxysulfate oxidation can be carried out under conditions that increase the solubility of VX and enhance the rate of decomposition.[11]

The rate of HD hydrolysis is also limited by low aqueous solubility, and this situation is aggravated where inadequate water, inadequate mixing, or when high HD concentrations are present. In these cases thiodiglycol, HD polymers, and assorted sulfonium salts concentrate at the HD surface and inhibit further dissolution.[13] All of these situations readily occur in soils, especially in arid regions where most chemical warfare agent production sites are located. Inhibition of HD solubility is not expected when

peroxysulfates are used because soluble sulfones are produced, and any HD polymers present at the HD/water interface, will be mineralized.

Peroxydisulfate oxidation has been likened to incineration since it can mineralize virtually all organic material. However, public opposition, a common problem with incineration projects, is expected to be significantly lower with a peroxydisulfate based technology due to low air emission levels.

1.3 Project Objectives

The goal of this study is to determine whether simulants of HD, GB, and VX can be adequately removed from soils. This was assessed in the following ways:

- By monitoring the kinetics of the simulant disappearance from solutions and soils.
- By monitoring the degradation of the peroxysulfate oxidants in the presence and absence of simulants and soil.
- By determining how specific the oxidants are for chemical warfare agent oxidation.
- By determining how much excess oxidant is required to overcome competitive reactions.
- By determining whether the concentrations of the simulant can be effectively reduced to levels below the detection limit of the analytical methods.
- When possible, determine whether the simulants are mineralized.

1.4 Approach

The project was carried out in three phases. In phase one, reactions in aqueous solution were investigated to acquire insight into the mechanisms surrounding the degradation of chemical warfare agents by peroxysulfate compounds, and to acquire rate data for comparison with the rates of reaction in soil systems. During phase I, aqueous solutions of chloroethyl ethylsulfide (CEES) and chloroethyl phenylsulfide (CEPSI) (simulants for HD), DIMP (simulant for GB), and O-ethyl S-ethyl phenylphosphonothioate (simulant for VX) were exposed to the oxidants peroxydisulfate ($S_2O_8^{2-}$) and peroxymonosulfate (HSO_5^-). Reaction rates for simulant disappearance in solution was obtained by analyzing the reaction solution with gas chromatography, ion chromatography, and high performance liquid chromatography. Reaction products and intermediates were either detected or it was confirmed that the simulants were completely mineralized (degraded to CO_2, PO_4^{3-}, Cl^- and SO_4^{2-}). The results of reactions between the simulants and peroxymonosulfate and peroxydisulfate were compared. The final product distributions, ability to mineralize the contaminants, and the effects of elevated temperatures were assessed. Comparisons between hydrolysis and peroxysulfate reaction rates were also made.

In the second phase, the degradation of chemical warfare agent simulant in soils was investigated to determine the ability of each oxidant to completely degrade chemical warfare agents in soil. During this phase, possible impediments to degradation in soil were investigated. The impact of soil sorption, agent insolubility, and competitive reactions with soil components were assessed. The soils were spiked with CEES, CEPSI, DIMP, or O-ethyl S-ethyl phenylphosphonothioate, slurried in peroxysulfate solutions, agitated, and periodically sampled. The soil slurries were analyzed for the parent contaminant and known degradation products. Degradation rates were compared with rates of hydrolysis, and the reaction time and peroxysulfate dose level requirements for complete contaminant degradation was determined. Comparisons were made between peroxymonosulfate and peroxydisulfate. Information was gathered on the ability of each

oxidant to completely degrade the simulant, requirements of elevated temperatures, and the susceptibility of each oxidant to scavenging side reactions with the soils. Rate data from phases I and II were compared to determine if the presence of soil retarded the rates of reaction by consuming oxidative equivalents or by strong sorption of the contaminant. The information obtained in phase II was used to recommend scale-up of the technology.

In the final phase, a conceptual design and construction cost estimate for a transportable batch demonstration unit was prepared. During this phase, data from the previous two phases was used to develop a conceptual design for a transportable batch demonstration plant. To develop a conceptual design, the research and engineering teams outlined a basic design, outlined design goals, contacted equipment vendors, and modified the design as vendor information was received. Upon completion of the conceptual design, a general set of equipment specifications and a process flow diagram was evaluated and a conceptual cost estimate for constructing the facility was developed. Upon completion of the cost estimate, a final process description was written.

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SECTION 2

MATERIALS AND METHODS

2.1 Materials

All experiments were carried out in 18 MΩ water. Oxone, ammonium peroxydisulfate, sodium peroxydisulfate, and potassium peroxydisulfate were purchased from Aldrich Chemical Company and used as received.

The soil selected for the study was a clean sandy loam soil from the TVA reservation in Muscle Shoals, Alabama. The soil was dried, ground, and passed through a 2 mm screen. Analysis by the ASTM D422 hydrometer method found: 9.4 percent clay, 17.7 percent silt, and 72.9 percent sand (USDA specifications).

Chemical analysis found:

Component or Characteristic	Weight % or pH	Component	Weight %
pH	pH 4.8	Total Organic Carbon	1.9 %
Water	2.6 %	Total Nitrogen	0.1 %
Iron	2.0 %	Aluminum	2.8 %
Silicon	33.2 %	Calcium	0.2 %
Magnesium	0.1 %	Phosphorus (as P_2O_5)	0.2 %

2.1.1 HD Simulant and Related Chemicals

Chloroethyl ethylsulfide (CEES), chloroethyl phenylsulfide (CEPSI), thiodiglycol (TDG), chloroethyl phenylsulfoxide (CEPSX), hydroxyethyl phenylsulfoxide (HEPSX), chloroethyl phenylsulfone (CEPSO), hydroxyethyl phenylsulfone (HEPSO), and phenyl vinylsulfone (PVSO) were purchased from Aldrich Chemical Company and used as received.

2.1.2 GB Simulant and Related Chemicals

Diisopropyl methylphosphonate (DIMP), methylphosphonic acid (MPA), and potassium hydrogen phosphate were purchased from Alfa/Aesar Johnson Matthey Corporation. All chemicals were used as received.

2.1.3 VX Simulant and Related Chemicals

Phenylphosphonic acid, potassium hydrogen phosphate, dicyclohexyamine, dichlorophenylphosphine, ethanol, iodoethane, benzene, dichloromethane, diethylether, sulfur, and pyridine were purchased from Aldrich Chemical Company.

2.1.3.1 Preparation of the VX Simulant O-ethyl S-ethyl Phenylphosphonothioate (OSDEPPT)

O-ethyl S-ethyl phenylphosphonothioate was prepared by literature methods.[1] A solution of ethanol (18 mL) and pyridine (15.3 mL) in 30 mL benzene was added dropwise to a stirring cooled solution of dichlorophenylphosphine (20.7 mL) in 175 mL benzene. After one hour, the precipitated pyridinium salt was removed by filtration. Water (75 mL) was added dropwise to the filtrate. The organic phase was separated and extracted with a saturated aqueous sodium bicarbonate solution. The aqueous phase was back extracted twice with dichloromethane. The combined organic phases were dried with anhydrous

sodium sulfate. The solvent was removed by rotary evaporation to give O-ethyl phenylphosphinate (IR (cm^{-1}): 2340 (ν_{P-H}), 1240 ($\nu_{P=O}$)).

Elemental sulfur (3.1 g, 0.097 mol) was slowly added to a stirred solution of O-ethyl phenylphosphinate (16.5 g, 0.097 mol) and dicyclohexylamine (17.6 g, 20 mL, 0.097 mol) in 200 mL diethylether. After stirring for 3 hours, the mixture was filtered and the solid recrystallized from hot ethyl acetate to yield 23.7 g dicyclohexylammonium O-ethyl hydrogen phenylphosphonothioate (mp: 152-153 °C).

Excess iodoethane (2.4 mL) was added to a stirred solution of 5.04 g dicyclohexylammonium O-ethyl hydrogen phenylphosphonothioate in 60 mL benzene. The solution was stirred for six days before the precipitate was removed by filtration. The benzene was removed from the filtrate to yield a viscous oil. The oil was purified by vacuum distillation to give O-ethyl S-ethyl phenylphosphonothioate (^1H NMR data ($CDCl_3$): δ 1.15 (t, 3H), 1.4 (t, 3H), 2.7 (q, 2H), 4.2 (q, 2H), 7.3-8.0 (m, 5H). And Mass Spec. data m/e: 230, 170, 141, 105, 77, 51).

2.1.3.2 Preparation of O-ethyl Phenylphosphonate for the Production of OSDEPPT

O-ethyl phenylphosphonic acid was prepared by the hydrolysis of O-ethyl phenylphosphinate. O-ethyl phenylphosphinate (5 g, 0.029 moles) was added to 150 mL water. A 50 % aqueous NaOH solution was slowly added until a pH of 14 was reached. The mixture was stirred for several hours until a homogeneous solution was obtained. The solution was acidified with HCl then extracted three times with chloroform. The organic phases were combined and the chloroform evaporated to leave an oil. The oil was dissolved in a minimum volume of benzene and 6 mL (0.029 mol) dicyclohexylamine was added. White crystals of dicyclohexylammonium O-ethyl phenylphosphonate formed and were recrystallized in hexane (mp = 140 °C). (NMR data: δ 1.1 (m, 7 H), 1.6 (m, 12 H), 2.1 (d, 4H), 2.95 (m, 2H), 7.2-7.9 (m, 5H)).

2.2 Analytical

2.2.1 Sampling

Samples were taken periodically from each reaction solution. Approximately 5 mL of the aqueous solution or soil slurry was transferred from the reaction vessel to an 8 ml glass sample vial using a glass pipette and allowed to cool in an ice bath. Approximately 4 mL was filtered using a 0.45 μm nylon filter and reserved for analysis by high performance liquid chromatography (CEES, CEPSI, and their degradation products), ion chromatography (chloride, chlorate, phosphate, methylphosphonic acid, phenylphosphonic acid) and Raman spectroscopy (peroxymonosulfate, peroxydisulfate, hydrogen peroxide, and sulfate). In the GB and VX simulant degradation studies a 0.1 g sample of the remaining solution was extracted with 2.5 g ethyl acetate and the organic phase was injected into the GC for analysis of DIMP and OSDEPPT.

2.2.2 Gas Chromatography

The GB simulant, diisopropyl methylphosphonate, and VX simulant, O-ethyl S-ethyl phenylphosphonothioate, were analyzed by gas chromatography with phosphorus specific detection using Methods AP-0048 and AP-0049. The system was comprised of a Varian 3400 GC with a thermionic Specific Detector, Model 1041 Universal Injector, and a 15 m DB5 megabore capillary column.

The products from chloroethyl ethylsulfide oxidation (chloroethyl ethyl sulfoxide, chloroethyl ethyl sulfone, hydroxyethyl ethyl sulfoxide, and hydroxyethyl ethyl sulfone) were analyzed by gas chromatography with mass spectroscopic detection.

2.2.3 High Performance Liquid Chromatography

The HD simulants chloroethyl ethylsulfide (CEES), chloroethyl phenylsulfide (CEPSI), and their degradation products, were analyzed by HPLC Method AP-0051. The system was comprised of the following components: Dionex GPM-2 gradient pump, Hewlett Packard Series 1050 MWD detector (210 nm), Valco 6-port injector, 150 x 4.6 mm Supelco Supelcosil C-18 ODS column, and a Hewlett Packard 3390A Integrator. A mobile phase of 50% methanol/50% water was used for all analytes but CEPSI. Analysis of CEPSI was performed using a mobile phase of 80% methanol/50% water.

2.2.4 Ion Chromatography

Ion chromatography was used to monitor break down products from treatment of simulants of HD (CEES & CEPSI), GB (DIMP), and VX (OSDEPPT) with peroxymonosulfate (Oxone) and peroxydisulfate. Analyses for chloride, chlorate, methylphosphonic acid, phenylphosphonic acid, ethyl phenylphosphonic acid, and phosphate was performed using Method AP-0053. The analytical system used was a Dionex Ion Chromatography system consisting of a 2120 Automated IC module, advanced IC module, analytical pump, Ionpac AS4A 4x250mm anion column, Ionpac AG4A 4x50mm guard column, AMMS-1 anion suppressor, conductivity detector, and 1.8 mM Na_2CO_3/1.7 mM $NaHCO_3$ mobile phase.

Due to the very large concentrations of sulfate present in concentrated Oxone solutions or aged peroxydisulfate solutions, changes in retention times may occur. To overcome the sulfate interferences, the sulfate is removed as $BaSO_4$ by passing each sample through an Alltech Maxi-clean IC-Ba cartridge prior to injection. The barium extraction had no effect on the recovery of any of the tested analytes.

2.2.5 Raman Spectroscopy

Raman spectroscopy was used to quantify and speciate the oxidants present in solution. Quantitation was based on the areas under the peaks from the O-O and S=O stretching vibrations for HSO_5^- (884, 1062 cm^{-1}) and $S_2O_8^{2-}$ (840, 1078 cm^{-1}), and the O-O stretch for H_2O_2 (890 cm^{-1}) – see Method AP-0050. Material balance could be obtained by quantifying the amount of SO_4^{2-} (S=O, 984 cm^{-1}) in solution after reduction of the oxidants.

The excitation source was a Spectra-Physics Stabilite 2017 argon ion laser operated at 514.5 nm. The optical path included a 3 nm bandwidth interference filter (Oriel) and a Lyot-wedge depolarizer (Oriel). The sample was contained in a 10 mm path length quartz cell (Starna Cells, Inc., model 30F). The laser beam was focused to the middle of the cell with a 100 mm focal length best-form laser lens (Oriel). The laser output was adjusted to 630 mW, measured immediately before the focusing lens. The signal was collected by a SPEX 1700F fiber optic collection system fitted with a focusing beam probe (Oriel model 77662). The signal was analyzed by a SPEX 1404 0.85 m double spectrometer equipped with a Hamamatsu R928P photomultiplier tube contained in a refrigerated housing. Signal averaging and data analysis were done using SPEX Spectramax software. All spectra were run with a resolution of 2 wavenumbers.

2.3 Procedures

2.3.1 Degradation of Peroxysulfates

Peroxysulfates decompose in water. In this series of experiments, peroxysulfate solutions were monitored to obtain the rate of peroxysulfate decomposition in water and soil slurries. These rates were later compared with the peroxysulfate decomposition rate when simulated chemical warfare agents are present.

2.3.1.1 Degradation of Peroxydisulfate

Aqueous solutions of potassium peroxydisulfate were prepared by equilibrating 100 mL deionized water to 90, 60, or 25 °C and adding 2 g $K_2S_2O_8$. The solutions were stirred, kept at constant temperature, and periodically sampled for analysis by Raman spectroscopy for peroxymonosulfate, peroxydisulfate, hydrogen peroxide, and sulfate. The sampling rate depended on the rate of reaction. Samples were taken every 30 minutes for the 90 °C reactions, but only once a day for reactions carried out at lower temperatures. The same experimental procedure was repeated for mixtures of 10 percent by weight sand and water, Kaolin clay and water, and soil and water.

2.3.1.2 Degradation of Peroxymonosulfate

Aqueous solutions of potassium peroxymonosulfate were prepared by equilibrating 100 mL deionized water to 25 °C and adding 6.14 g Oxone. The solutions were stirred, kept at constant temperature, and periodically sampled for analysis by Raman spectroscopy for peroxymonosulfate, peroxydisulfate, hydrogen peroxide, and sulfate. The same experimental procedure was repeated for a mixture of 10 percent by weight soil and water.

2.3.2 HD Simulant Degradation

2.3.2.1 Hydrolysis of Chloroethyl Phenylsulfide (CEPSI) in Aqueous Solutions

Two samples of deionized water were equilibrated in thermostatted water baths to 22 °C. The pH of one sample was adjusted to 2.8 (the pH of a typical Oxone solution) with dilute sulfuric acid, and the pH of the other was adjusted to 5.0 (the typical pH of a potassium peroxydisulfate solution). Chloroethyl phenylsulfide (14 mg) was added directly to 100 mL of each solution and samples of the aqueous phase were taken hourly

and injected directly onto a HPLC and analyzed for chloroethyl phenylsulfide, and it's degradation products. The same experiment was repeated at 60 °C.

2.3.2.2 Peroxysulfate Oxidation of Chloroethyl Ethylsulfide (CEES) in Aqueous Solutions

Aqueous solutions were prepared by the direct addition of 30 mg CEES to 250 mL deionized water. As was the case for CEPSI, complete dissolution and hydrolysis of the CEES had occurred after stirring for several hours. Three samples were prepared from the spiked solution. One of the samples (50 mL) served as a control, another had 0.01 g potassium peroxymonosulfate added to 100 mL, and the third sample had 0.01 g ammonium peroxydisulfate added to the final 100 mL. In one experiment the samples were thermostatted to 22 °C. The experiment was then repeated at 60 °C. Periodically samples were removed and injected directly onto the HPLC for analysis of CEES and HEES. Samples were saved at the end of the reactions for additional product identification by GC/MS.

2.3.2.3 Peroxysulfate Oxidation of Chloroethyl Phenylsulfide in Aqueous Solutions

Stoichiometric Concentrations of Oxidants

In order to follow the stepwise room temperature degradation of the chloroethyl phenylsulfide, equimolar concentrations of the peroxysulfates oxidants and CEPSI were added to water. During this procedure two 500 mL aqueous solutions containing deionized water were prepared. The first contained 0.16 g Oxone (1.0 mM peroxymonosulfate), the second contained 0.059 g (0.5 mM) ammonium peroxydisulfate. Equimolar concentrations of CEPSI (0.5mM or 0.4 g) were added to each of the stirred solutions. Samples of the aqueous phase were taken after the initial 30 minutes of reaction time, then hourly for the first day. An additional sample was taken after 24 hours. In the case of peroxydisulfate, the reaction was sufficiently slow that samples were taken every few days for the next three weeks before the reaction was complete.

Each sample was injected directly onto the HPLC and analyzed for chloroethyl phenylsulfide and it's degradation products.

Excess Oxidants

An aqueous solution was prepared by adding 0.059 g (0.67 mM) CEPSI to 500 mL of deionized water. Six 40-mL samples of the stock solution were taken. Three were equilibrated to 60 °C on a thermostatted water bath and the other three were left at room temperature (22 °C). At each temperature, one sample was left as a control, one sample had 0.04 g Oxone (0.1% Oxone; 3.3 mM peroxymonosulfate) added and the third had 0.04 g ammonium peroxydisulfate (0.1%; 4.4 mM) added. Each sample was periodically analyzed by HPLC for CEPSI, CEPSI oxidation products, and CEPSI hydrolysis products. Samples were taken every half hour for the first 3 hours, then hourly the first day. An additional sample was taken after 24 hours to ensure the reaction was complete.

2.3.2.4 Peroxysulfate Oxidation of Chloroethyl Phenylsulfide in Slurries Containing Spiked Soils

Attempts were made to spike soils with hexane, acetone, or methanol solutions of CEES and CEPSI. Extraction of the soil and HPLC analysis gave unacceptably low (0 - 4 percent) recoveries. Apparently the CEES and CEPSI were volatilizing with the solvents. Adding the CEES or CEPSI directly to the soil, mixing well, and extracting with acetonitrile gave reproducible recoveries of 95 percent or better.

CEPSI (17.5 mg) was added to 50 g soil. The spiked soil was separated into three 10 g samples. The first sample was slurried in 100 mL water, the second was slurried in 100 mL of a 0.1 percent Oxone solution, and the third was slurried in 100 mL of a 0.1 percent ammonium peroxydisulfate solution. Samples were taken periodically from each solution and analyzed by HPLC (for CEPSI and it's degradation products) and IC (for chloride and chlorate). This experiment was repeated at ambient temperature, 60 °C, and 75 °C.

In each case the initial phase of the reaction was fast and samples were taken every half hour. After 3 hours, the sampling rate was reduced to once an hour. The reactions that were not completed in one day were sampled once more after four days.

2.3.3 GB Simulant Degradation

2.3.3.1 Hydrolysis of Diisopropyl Methylphosphonate (DIMP) in Aqueous Solution

An aqueous stock solution of DIMP (100 ppm or 0.5 mM) was prepared for each experiment. The solution was split into a control sample and samples to which various levels of oxidant were added. The control sample was subjected to the same reaction conditions as the oxidant-containing solutions. Periodically, analytical samples of the control sample were taken and extracted with ethyl acetate. The organic phase was analyzed for DIMP by GC. Complete recovery (>96 %) of the DIMP could be obtained regardless of the solution pH, temperature, or sampling time. The DIMP was stable in aqueous solution and hydrolysis or volatilization did not occur during the time frames of the experiments (seven hours).

2.3.3.2 Peroxysulfate Degradation of Diisopropyl Methylphosphonate in Aqueous Solutions

Six 50-mL aqueous solutions of DIMP (100 ppm or 0.5 mM) were prepared. Three of the solutions were held at 22 °C, and the remaining solutions were equilibrated to 60 °C. At each temperature one solution had no oxidant added, another had 0.05 g Oxone (3mM HSO_5^-) added, and the third had 0.25 g $Na_2S_2O_8$ (20 mM) added. Each reaction was sampled every half hour until the DIMP was degraded below detection limits, then sampled hourly to monitor the methylphosphonate and phosphate reaction products. The samples were split in half. One part of the sample was analyzed by IC (phosphate and methylphosphonic acid), the other was extracted with ethyl acetate and the organic phase was analyzed for DIMP by GC.

2.3.3.3 Peroxysulfate Degradation of Diisopropyl Methylphosphonate in Slurries Containing Spiked Soils

A 10% aqueous soil slurry was prepared using 1000 ppm DIMP spiked soil. The mixture was equilibrated to either 60 °C or 90 °C on a thermostatted sand bath. Various amounts of peroxydisulfate were added to the bottles. The 60 °C experiments were performed with peroxydisulfate concentrations of 1 percent. The 90 °C samples had peroxydisulfate concentrations of 1, 2 and 3.8 percent by weight. The mixtures were stirred continuously and sampled periodically. The initial phase of the reaction was rapid so samples were taken as often as possible (5, 10, 30, and 60 minutes). The reaction was nearly complete after one hour so the sampling rate was reduced to every half hour for the next several hours. Part of each sample (2 g) was extracted with ethyl acetate and analyzed for DIMP by GC. The remainder of the samples were filtered and the aqueous phase analyzed by IC (for phosphate and methylphosphonic acid) and Raman spectroscopy (for peroxymonosulfate, peroxydisulfate, hydrogen peroxide, and sulfate).

2.3.4 VX Simulant Degradation

The reaction with Oxone was not attempted in soil slurries since the aqueous phase results showed no reaction between peroxymonosulfate and DIMP.

2.3.4.1 Hydrolysis of O-ethyl S-ethyl Phenylphosphonothioate in Aqueous Solutions

A solution that consisted of 10 mM in O-ethyl S-ethyl phenylphosphonothioate (OSDEPPT) and 100 mM in NaOH was stirred and sampled after 1, 10, 20, 30, 60, and 90 minutes of reaction time. The samples were immediately extracted with ethyl acetate and analyzed for OSDEPPT by GC.

2.3.4.2 Peroxysulfate Oxidation of O-ethyl S-ethyl Phenylphosphonothioate in Aqueous Solutions

Six 100-mL aqueous solutions of OSDEPPT (5 mM) were prepared. Three of the solutions were held at 25 °C, and the remaining solutions were equilibrated to 90 °C. At each temperature, one solution had no oxidant added, another had 1.5 g Oxone (100 mM HSO_5^-) added, and the third had 2.7 g $K_2S_2O_8$ (100 mM) added. Each reaction was sampled as rapidly as possible during the initial hour of reaction, and the samples were stored on ice to minimize the amount of reaction occurring between sampling and analysis. Additional samples were taken every half hour or hourly for the next several hours. The analytical samples were split in half. One part of the samples was analyzed by IC (for phosphate and phenylphosphonic acid), the other was extracted with ethyl acetate and the organic phase was analyzed for OSDEPPT by GC.

2.3.4.3 Peroxysulfate Oxidation of O-ethyl S-ethyl Phenylphosphonothioate in Slurries Containing Spiked Soils

Four soil samples were prepared by spiking each soil (10 g) with 0.0115 g OSDEPPT and adding 100 mL water. Two of the mixtures were equilibrated at 25 °C and the other samples were equilibrated to 90 °C on a thermostatted sand bath. Potassium peroxydisulfate (2.7 g; 100 mM) was added to one of the 90 °C mixtures and Oxone (6.1g; 100mM) was added to one of the 25 °C mixtures. The mixtures were stirred continuously and sampled periodically for analysis. Each reaction was sampled as rapidly as possible during the initial hour of reaction, and the analysis samples were stored on ice to minimize the amount of reaction occurring during the time between sampling and analysis. Additional samples were taken every half hour or hourly for the next several hours. Part of each sample was extracted with ethyl acetate and analyzed for OSDEPPT by GC. The remainder of the samples were filtered and the aqueous phase analyzed by IC (for phosphate and phenylphosphonic acid) and Raman spectroscopy (for peroxymonosulfate, peroxydisulfate, hydrogen peroxide, and sulfate).

2.4 References

[1] (a) Berg, F. J.; et al. *Langmuir* **1995**, *11*, 411-413. (b) DeBruin, K. E.; et al. *J. Am. Chem. Soc.* **1989**, *111*, 5871.

SECTION 3

RESULTS AND DISCUSSION

3.1 Decomposition of Peroxysulfate Compounds in Aqueous Solution and Soil Bearing Slurries

Peroxysulfate compounds are strong oxidants. The formal oxidation potentials (versus Normal Hydrogen Electrode (NHE)) are 1.81 V for peroxymonosulfate,[1] and 2.01 V for peroxydisulfate,[2] and the sulfate radical anion is an even stronger oxidizing agent. In order to assess whether peroxysulfate compounds have practical application toward soil remediation, some understanding of the selectivity of the various oxidants toward oxidation of the target compounds is needed. This information was obtained both by observing whether chemical warfare agent simulants were completely degraded in soil slurries after exposure to peroxysulfate compounds, and by observing the relative rates of the oxidant's decomposition in the presence of water, soil, and CWA simulant.

3.1.1 Decomposition of Peroxydisulfate

Peroxydisulfate degrades in aqueous solution by two competitive reactions.[3] In acidic solutions peroxydisulfate degrades to peroxymonosulfate, equation 1. This reaction is in competition with a pH independent, temperature dependent reaction involving the cleavage of the peroxide bond, equation 2. The sulfate radical anions produced in this reaction are extremely strong oxidants and are often the active oxidant in peroxydisulfate reactions.

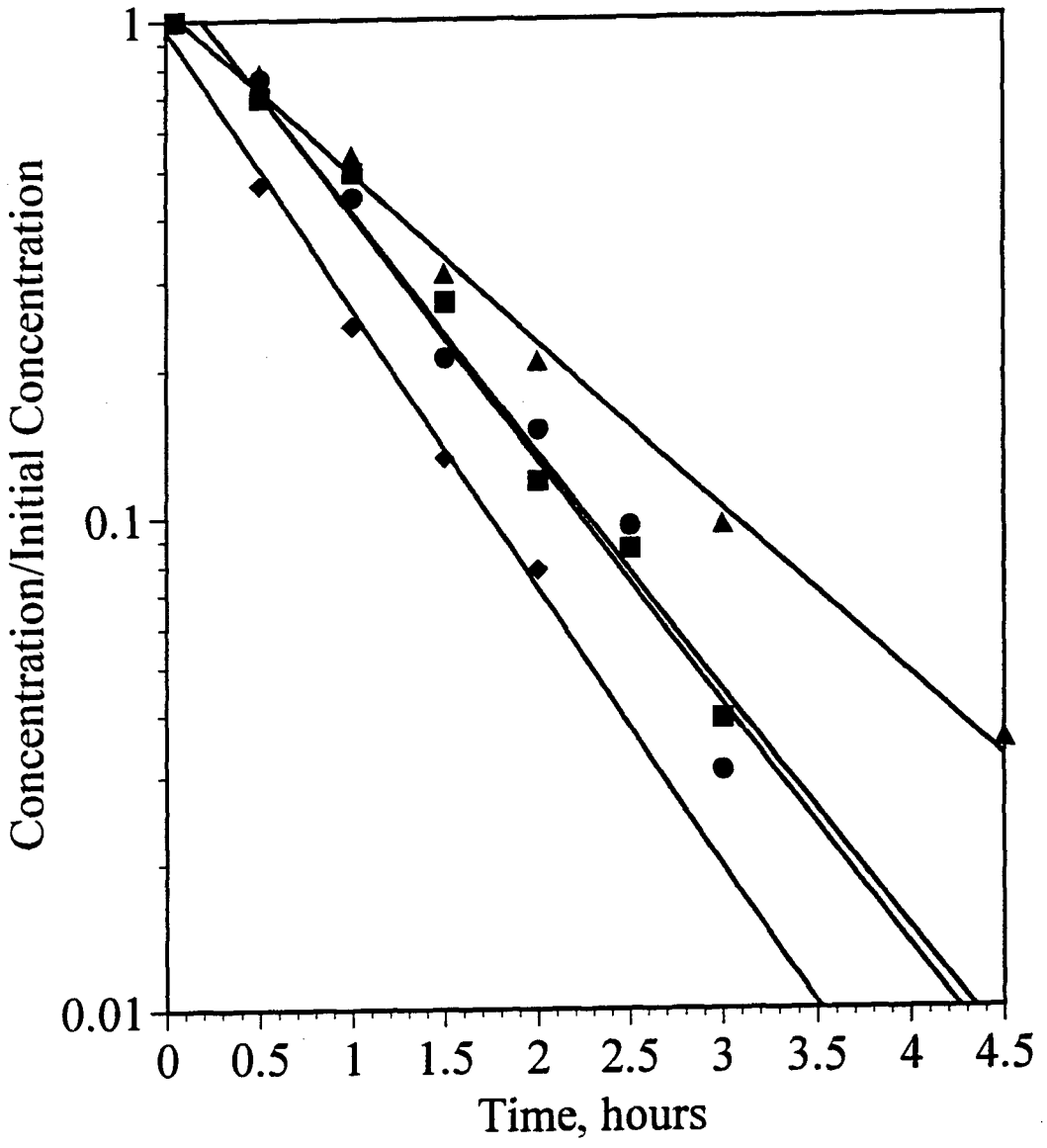
$$HS_2O_8^{1-} + H_3O^+ \rightarrow H_2SO_5 + H_2SO_4 \quad (1)$$

$$S_2O_8^{2-} \rightarrow 2\ SO_4^{\cdot-} \quad (2)$$

Literature values for the rate of peroxydisulfate decomposition in water depend on solution temperature, pH, and ionic strength. At 90 °C peroxydisulfate degradation rates range from 0.41 to 1.42 hr^{-1}.[4] Under TVA's experimental conditions, the rate of degradation of potassium peroxydisulfate in water at 90 °C was found to have a first order rate constant of 0.82 hr^{-1}, corresponding to a half life of 0.84 hr, Figure 3-1. When the experiment was repeated in a sand/water mixture and a Kaolin clay/water mixture, the rate of decomposition increased to 1.11 and 1.13 hr^{-1}, respectively. In a soil water mixture the rate increased to 1.28 hr^{-1} and the half life decreased to 0.54 hr. The effect of soil was less pronounced at 60 °C, Figure 3-2. The half life was 17 hours in water and 16 hours in an aqueous soil slurry. At room temperature the peroxydisulfate did not degrade appreciably either in soil or water over the experimental time frame.

3.1.2 Decomposition of Peroxymonosulfate

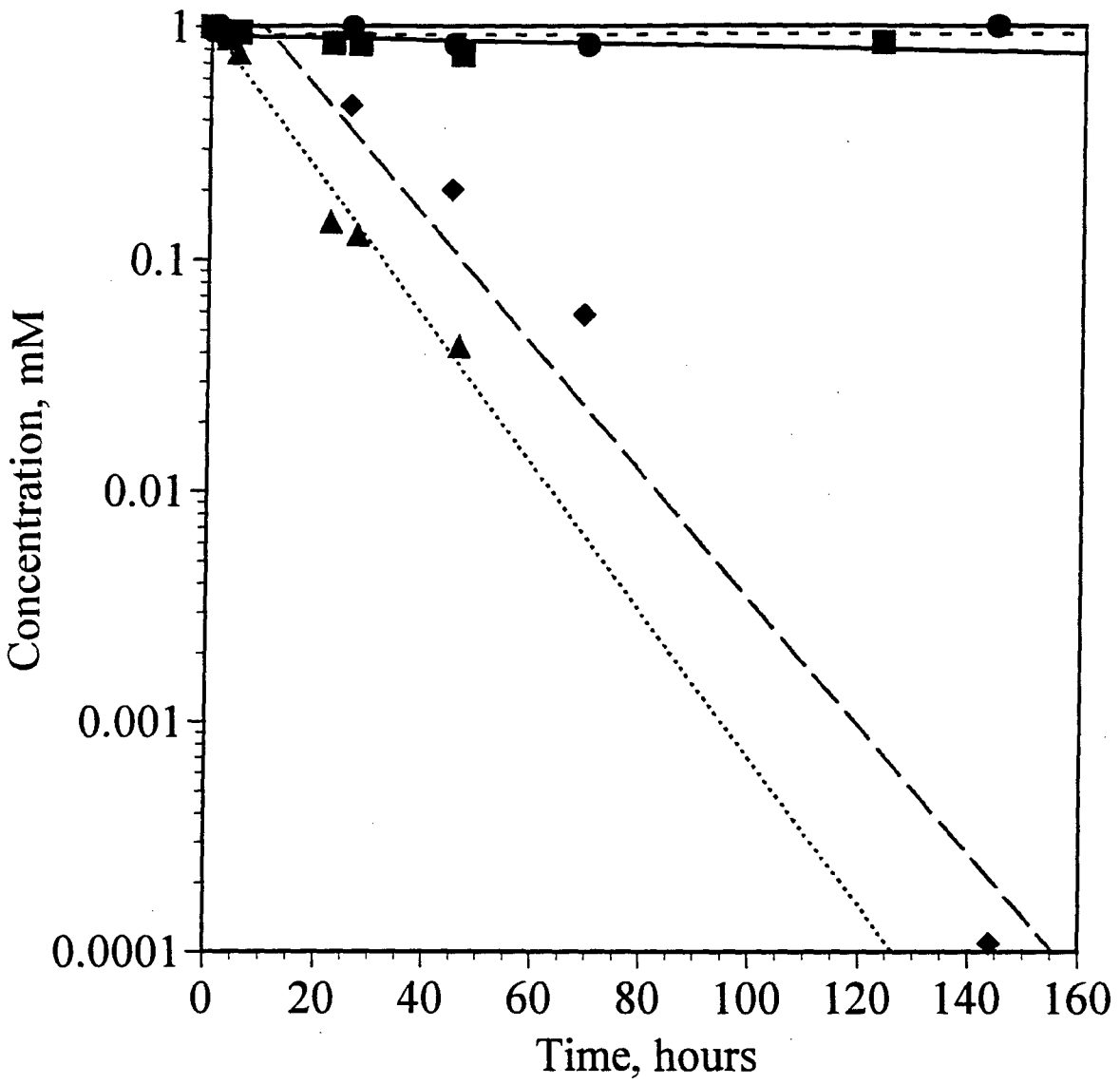
Peroxymonosulfate was stable over the experimental time frame, Figure 3-3. Even after 10 days, a constant peroxymonosulfate concentration was observed in solution. The presence of soil in the peroxymonosulfate solution had no observable effect. These peroxymonosulfate solutions were prepared by the addition of Oxone to the water or soil slurries. Oxone is DuPont's trade name for the triple salt 2 $KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$. Oxone was used because it is a stable powder that is easily and safely stored and handled. The sole active oxidant in Oxone is peroxymonosulfate, and the sulfate and bisulfate components of the salt buffer the reaction solution at a pH near 2.



Experiments were carried out in water (triangles), soil/water slurries (diamonds), sand/water slurries (squares), and Kaolin clay/water slurries (circles).

Figure 3-1

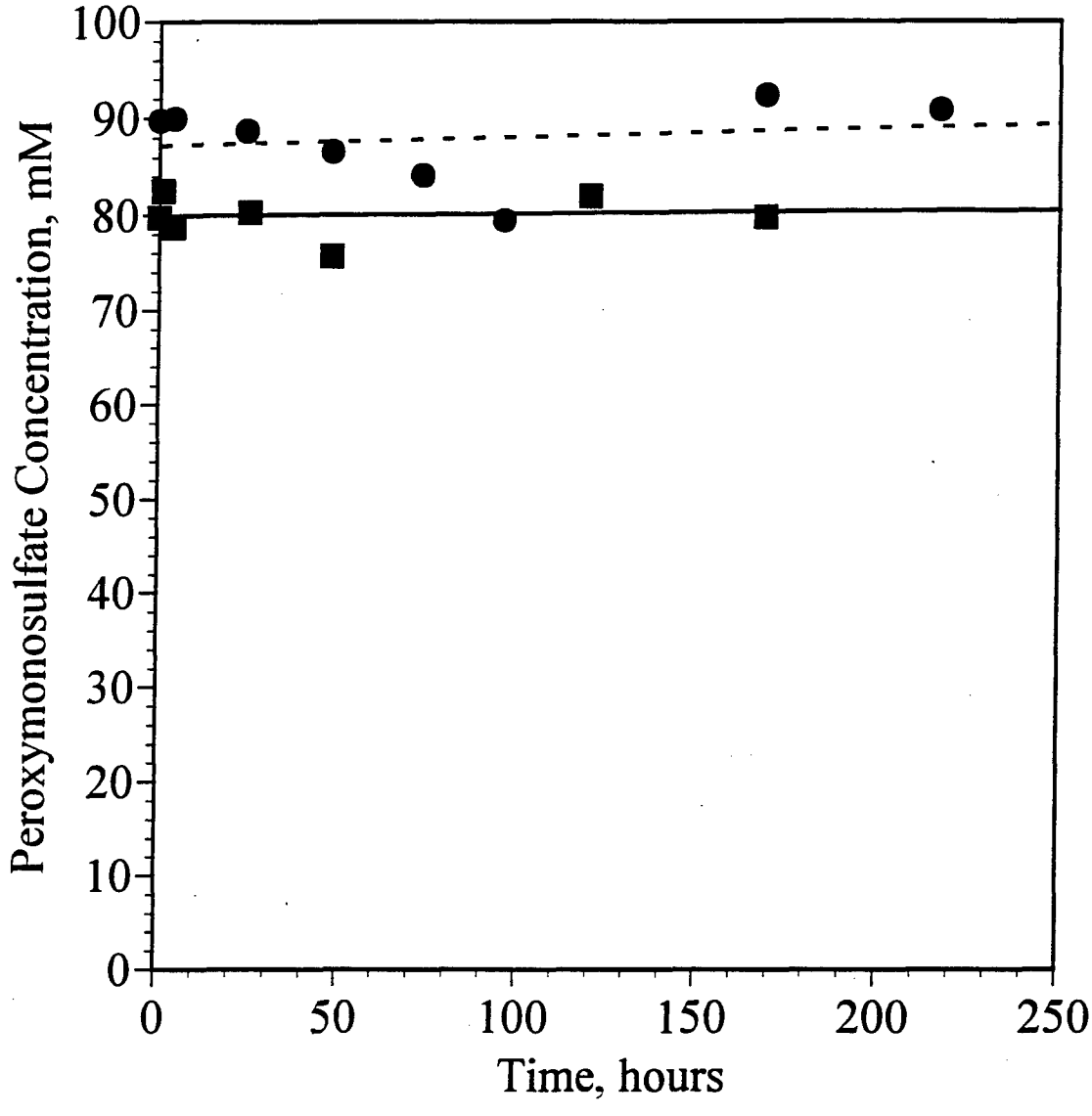
Decomposition of Peroxydisulfate in Aqueous Solutions at 90°C



Data represent concentrations of peroxydisulfate in 25°C water (circles), 25°C soil/water slurries (squares), 60°C water (diamonds), and 60°C soil/water slurries (triangles).

Figure 3-2

Decomposition of Peroxydisulfate in Aqueous Solutions at 25°C and 60°C



Data represent concentrations of peroxymonosulfate in deionized water (squares, dashed line) and soil slurries (circles, solid line).

Figure 3-3

Peroxymonosulfate in Aqueous Solutions and Soil Slurries Containing Oxone

3.2 Degradation of HD Simulants

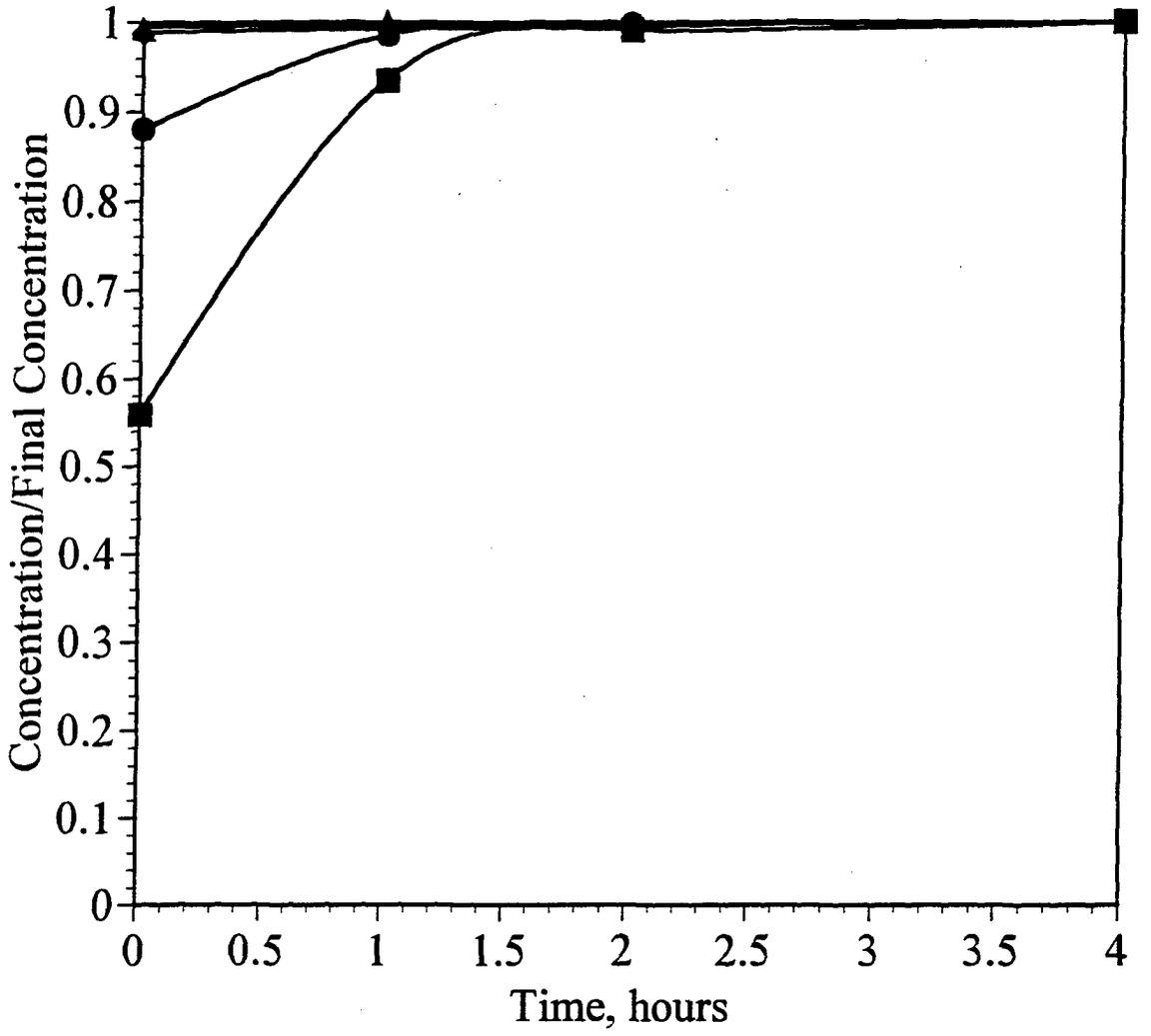
3.2.1 Hydrolysis of the HD Simulant Chloroethyl Phenylsulfide

Rapid hydrolysis to hydroxyethyl phenylsulfide ($C_6H_5SCH_2CH_2OH$ or HEPSI) occurred when 140 ppm (0.8 mM) of the HD simulant chloroethyl phenylsulfide ($C_6H_5SCH_2CH_2Cl$) was added to water, Figure 3-4. The concentration of hydroxyethyl phenylsulfide was observed to increase within the solution, but no chloroethyl phenylsulfide was ever observed in solution. These results are consistent with the behavior of HD ($ClCH_2CH_2SCH_2CH_2Cl$) in water.[5] HD is insoluble and slowly hydrolyzes by interfacial reactions as shown in equations 3 and 4.

$$ClCH_2CH_2SCH_2CH_2Cl \rightleftharpoons ClCH_2CH_2\text{-}S^{\oplus}\text{(}CH_2CH_2\text{)} \xrightarrow{OH^-} ClCH_2CH_2SCH_2CH_2OH \quad (3)$$

$$ClCH_2CH_2SCH_2CH_2OH + OH^- \rightarrow HOCH_2CH_2SCH_2CH_2OH + Cl^- \quad (4)$$

The concentration of hydroxyethyl phenylsulfide was observed to increase at rates that were dependent on both solution pH and temperature. At ambient temperature (22 °C) and the approximate pH of an Oxone solution (pH = 2.8), hydrolysis was retarded by the acidic conditions and the subsequent appearance of hydroxyethyl phenylsulfide was slow. However, even at low pH, hydrolysis was rapid relative to dissolution of chloroethyl phenylsulfide and no chloroethyl phenylsulfide was ever observed in solution. At ambient temperature and the approximate pH of soil (pH = 5.0), hydroxyethyl phenylsulfide appeared more rapidly than at pH 2.8. At 60 °C the conversion to hydroxyethyl phenylsulfide was nearly complete before the first sample could be analyzed in both the solutions at pH 2.8 and 5.0.



Data represent the concentration of hydroxyethyl phenylsulfide at various times after the addition of chloroethyl phenylsulfide at 22°C in a pH=2.8 solution (squares), 22°C in a pH=5.0 solution (circles), 60°C in pH=2.8 solution (diamonds), and 60°C in a pH=5.0 solution (triangles).

Figure 3-4

Hydrolysis of the HD Simulant Chloroethyl Phenylsulfide (CEPSI in Aqueous Solution

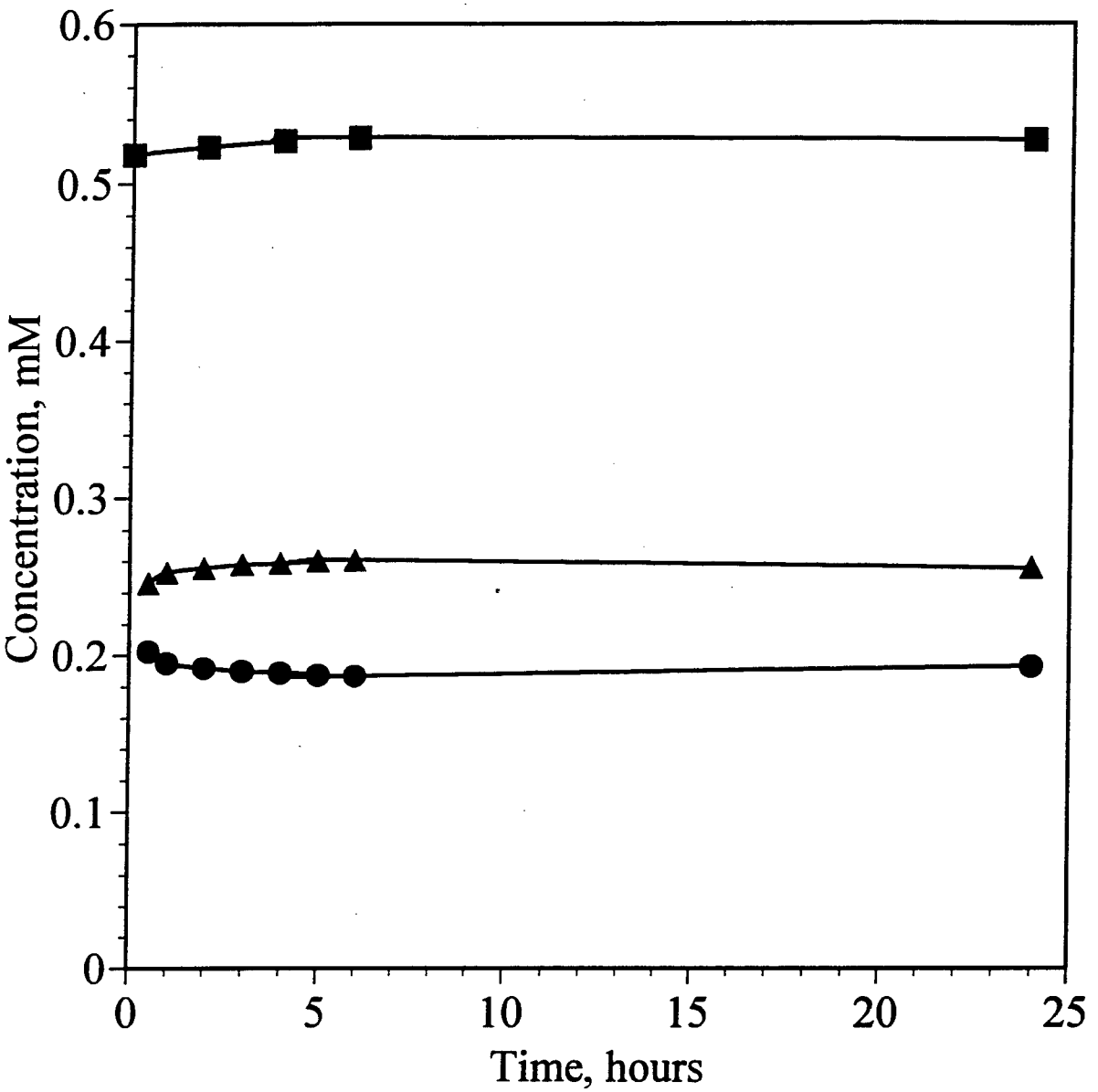
3.2.2 Oxidation of the HD Simulant Chloroethyl Ethylsulfide by Peroxysulfates in Aqueous Solution

In this experiment, 0.1 g/L of potassium peroxymonosulfate (Oxone) or ammonium peroxydisulfate were added to aqueous solutions containing 120ppm (1.1 mM) of the HD simulant chloroethyl ethylsulfide (CEES). As in the CEPSI hydrolysis experiments, the hydrolysis product hydroxyethyl ethylsulfide (HEES), was detected in the solution while the HD simulant remained in a separate non-aqueous phase. (The simulant phase was not sampled directly and its existence was inferred by the appearance of chlorinated reaction products chloroethyl ethylsulfoxide and chloroethyl ethylsulfone after oxidants were added to the mixtures). Within 3 hours of adding peroxydisulfate, the hydroxyethyl ethylsulfide was consumed. When the potassium peroxymonosulfate (Oxone) oxidant was used, the hydroxyethyl ethylsulfide was completely consumed before the first sample could be analyzed. Gas chromatography with mass spectroscopic detection confirmed that the degradation products chloroethyl ethylsulfone ($ClCH_2CH_2(CH_2CH_3)SO_2$) and hydroxyethyl ethylsulfone ($HOCH_2CH_2(CH_2CH_3)SO_2$) were formed. Analytical standards for these reaction products were not available, so no attempts to quantify them were made.

3.2.3 Oxidation of the HD Simulant Chloroethyl Phenylsulfide in Aqueous Solution

3.2.3.1 Oxidation of Chloroethyl Phenylsulfide When Added to a Solution Containing Stoichiometric Amounts of Peroxymonosulfate at Ambient Temperature (22 °C)

First an aqueous solution containing 85 ppm (0.5 mM) of the HD simulant chloroethyl phenylsulfide ($C_6H_5SCH_2CH_2Cl$) in water was analyzed by HPLC for chloroethyl phenylsulfide and it's degradation products, Figure 3-5. In the absence of added oxidants, rapid hydrolysis to hydroxyethyl phenylsulfide ($C_6H_5SCH_2CH_2OH$) was observed.



Data represent the concentration of the degradation products chloroethyl phenylsulfone (triangles), and hydroxyethyl phenylsulfone (circles) in a 0.5 mM aqueous solution of peroxymonosulfate at various times after addition of 0.5 mM of the HD simulant chloroethyl phenylsulfide. Squares represent the concentration of the simulants hydrolysis product, hydroxyethyl phenylsulfide, in the absence of peroxymonosulfate.

Figure 3-5

Oxidation of the HD Simulant Chloroethyl Phenylsulfide (CEPSI) with a Stoichiometric Amount of Oxone (Peroxymonosulfate) at Ambient Temperature (22 °C)

Next equal molar amounts of chloroethyl phenylsulfide and Oxone were added to water. Almost immediately, nearly equal amounts of chloroethyl phenylsulfone ($C_6H_5(CH_2CH_2Cl)SO_2$) and hydroxyethyl phenylsulfone ($C_6H_5(CH_2CH_2OH)SO_2$) were observed to form in solution, Figure 3-5. The observance of CEPSO implies that potassium peroxymonosulfate can react interfacially with chloroethyl phenylsulfide to form chloroethyl phenylsulfone before hydrolysis occurs to form hydroxyethyl phenylsulfide. The solution was monitored for 500 hours and no significant change was observed after the initial 24 hours.

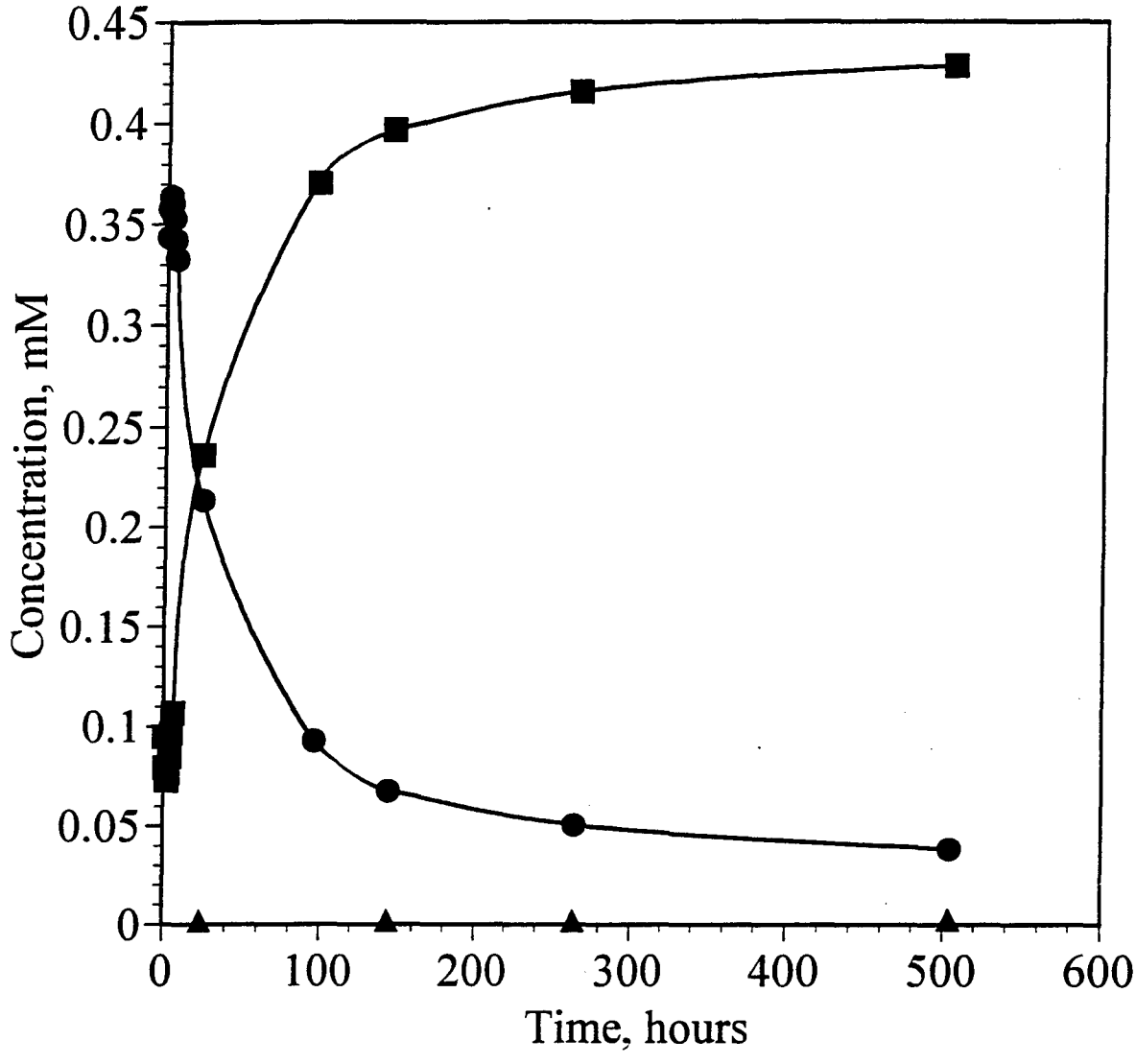
From the stability of chloroethyl phenylsulfone in solution it can be concluded that it is not readily hydrolyzed under the acidic conditions (pH=2.8) of the peroxymonosulfate solution. The absence of hydroxyethyl phenylsulfoxide ($C_6H_5S(O)CH_2CH_2OH$) or chloroethyl phenylsulfoxide ($C_6H_5S(O)CH_2CH_2Cl$) was surprising since they are the products of the initial oxidation of hydroxyethyl phenylsulfide and chloroethyl phenylsulfide, equation 5. Oxone, however, contains two equivalents of peroxymonosulfate, so sufficient oxidative equivalents were present in solution to convert the sulfoxides to sulfones, equation 6. Apparently Equation 6 is fast, relative to Equation 5.

$$C_6H_5SCH_2CH_2Cl + HSO_5^- \rightarrow C_6H_5S(O)CH_2CH_2Cl + HSO_4^- \quad (5)$$

$$C_6H_5S(O)CH_2CH_2Cl + HSO_5^- \rightarrow C_6H_5(CH_2CH_2Cl)SO_2 + HSO_4^- \quad (6)$$

3.2.3.2 Oxidation of Chloroethyl Phenylsulfide When Added to a Solution Containing Stoichiometric Amounts of Peroxydisulfate at Ambient Temperature (22 °C)

When equal molar (0.5 mM) amounts of the HD simulant chloroethyl phenylsulfide and ammonium peroxydisulfate were added to water, the chloroethyl phenylsulfide was immediately converted to chloroethyl phenylsulfone and a small amount of hydroxyethyl phenylsulfone, Figure 3-6. The chloroethyl phenylsulfone slowly hydrolyzed to hydroxyethyl phenylsulfone. The pH of the peroxydisulfate solution was higher (pH=5)



Data represent concentrations of the HD simulants' hydrolysis product hydroxyethyl phenylsulfide (triangles) and the degradation products chloroethyl phenylsulfone (circles), hydroxyethyl phenylsulfone (squares) at various times after addition of 0.67 mM chloroethyl phenylsulfide to a 0.67 mM aqueous solution of peroxydisulfate.

Figure 3-6

Oxidation of the HD Simulant Chloroethyl Phenylsulfide (CEPSI) with a Stoichiometric Amount of Peroxydisulfate at Ambient Temperature (22°C)

than the oxone solution and apparently encouraged slow hydrolysis. As in the case with Oxone, ammonium peroxydisulfate is able to supply two oxidative equivalents and oxidize chloroethyl phenylsulfide to chloroethyl phenylsulfoxide and on to chloroethyl phenylsulfone, equations 7 and 8.

$$C_6H_5SCH_2CH_2Cl + S_2O_8^{2-} \rightarrow C_6H_5S(O)CH_2CH_2Cl + SO_4^{\cdot-} + SO_4^{2-} \quad (7)$$

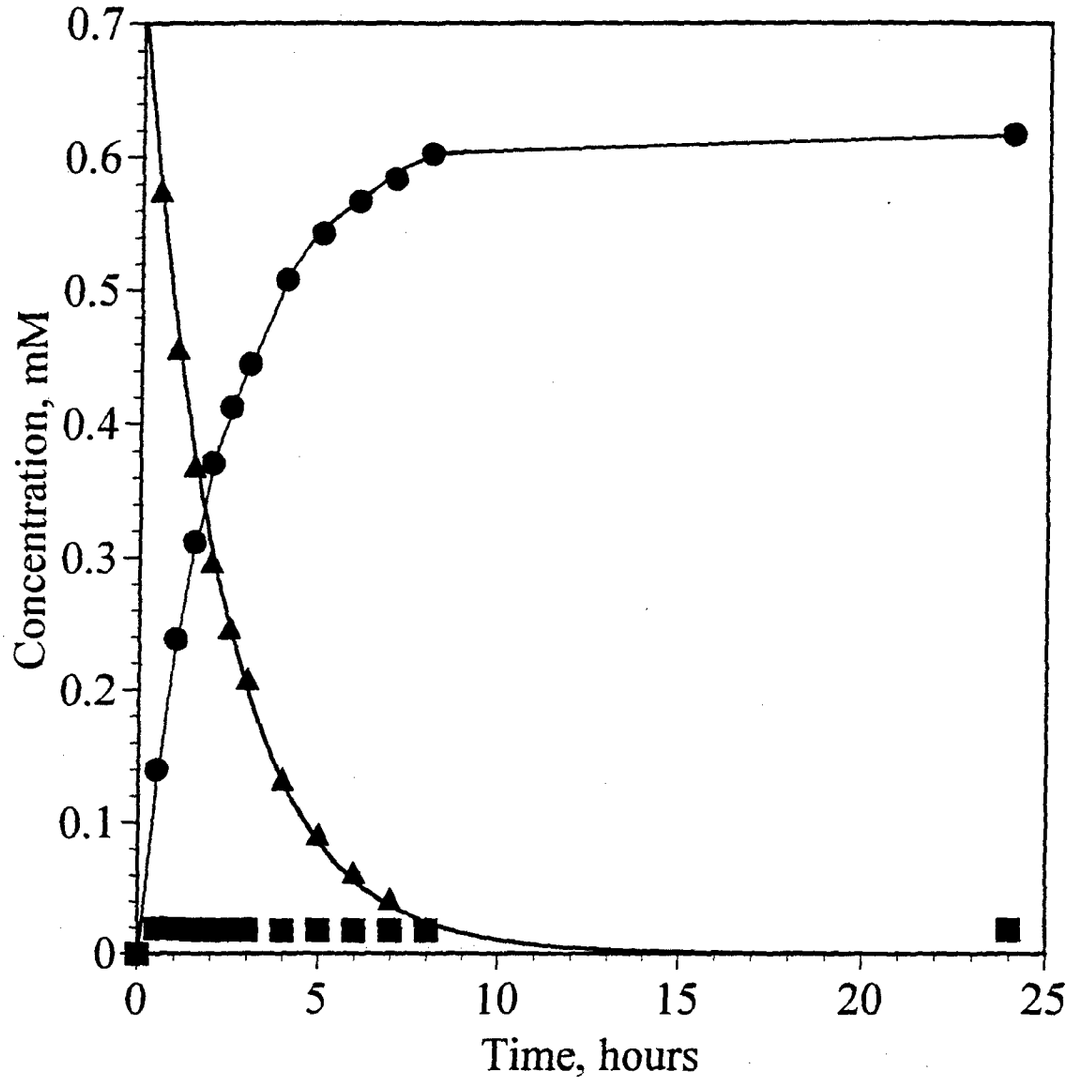
$$C_6H_5S(O)CH_2CH_2Cl + SO_4^{\cdot-} + SO_4^{2-} \rightarrow C_6H_5(CH_2CH_2Cl)SO_2 + 2\,SO_4^{2-} \quad (8)$$

3.2.3.3 Oxidation of Solutions Containing Hydroxyethyl Phenylsulfide (HEPSI) with Excess Peroxysulfate Oxidants at Ambient Temperature (22 °C)

Excess oxidants were added to aqueous solutions containing 120 ppm (0.67mM) of the HD simulant chloroethyl phenylsulfide. Sufficient time was allowed for the chloroethyl phenylsulfide to completely hydrolyze prior to addition of the oxidant. Therefore, hydroxyethyl phenylsulfide and not chloroethyl phenylsulfide, was the simulant being oxidized. The hydrolysis reaction was necessitated by the need for a homogeneous solution in order to obtain rates of reactions. The presence of chloroethyl phenylsulfide would have led to a two-phase system and kinetic complications due to adsorption/desorption and solubility equilibria.

In the presence of five fold excess (3.3 mM) of peroxymonosulfate (Oxone), rapid conversion of 0.67 mM hydroxyethyl phenylsulfide to hydroxyethyl phenylsulfone (0.63 mM) occurred before the first analytical sample could be taken.

In the presence of a 6.6 fold excess of peroxydisulfate (4.4 mM), 0.67 mM hydroxyethyl phenylsulfide degraded at a rate of 0.42 hr^{-1} and hydroxyethyl phenylsulfone appeared as the predominant reaction product (0.62 mM), Figure 3-7. It was observed that the oxidation rate of chloroethyl phenylsulfide, with a stoichiometric amount of peroxydisulfate, was substantially greater than that for the oxidation of hydroxyethyl



Data represent concentrations of the HD simulants' hydrolysis product hydroxyethyl phenylsulfide (triangles), and the degradation products hydroxyethyl phenylsulfoxide (squares), and hydroxyethyl phenylsulfone (circles) at various times after addition of 3.7 mM peroxydisulfate to a 0.67 mM aqueous chloroethyl phenylsulfide (CEPSI) solution.

Figure 3-7

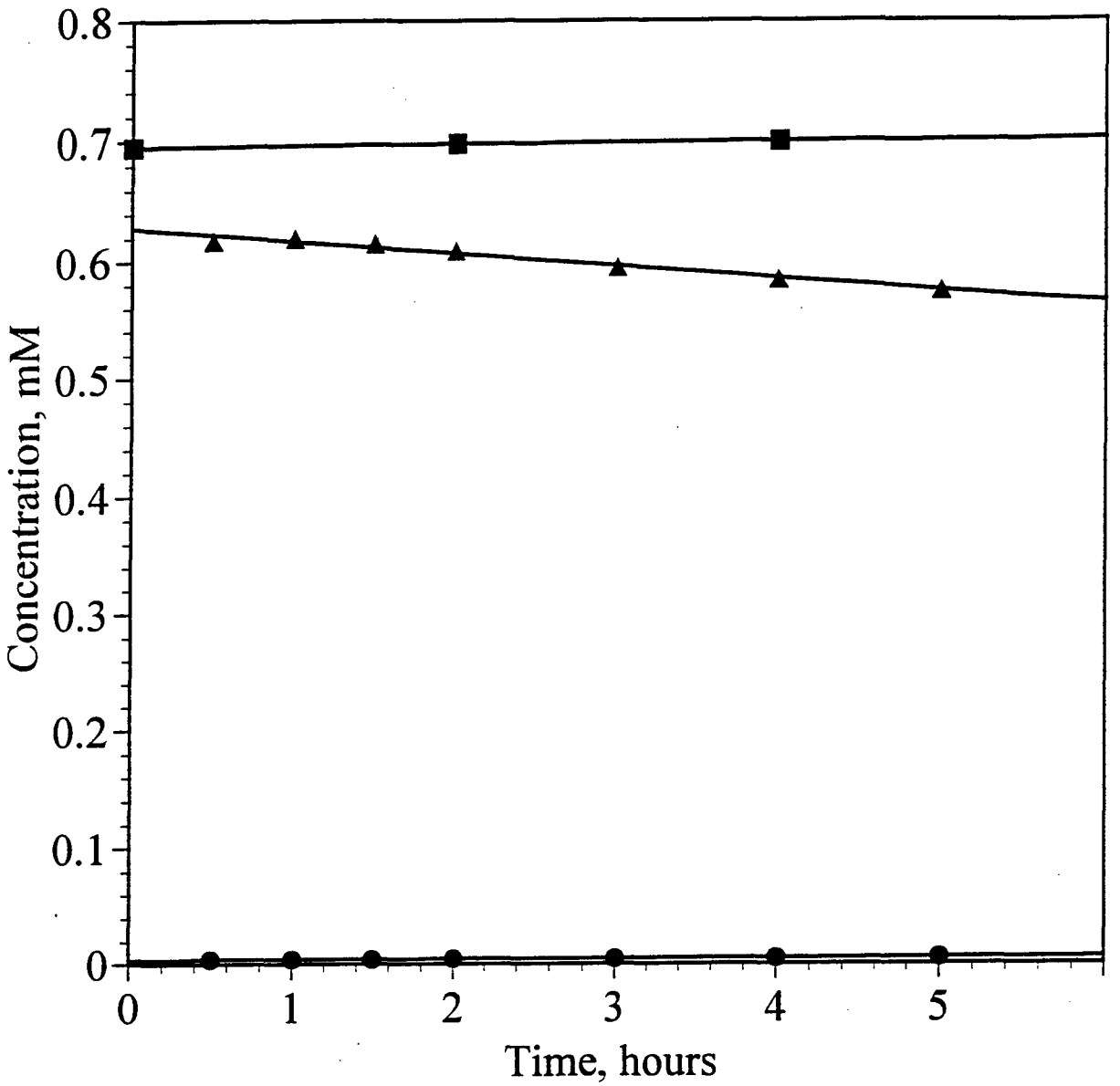
Oxidation of HD Simulants' Hydrolysis Product Hydroxyethyl Phenylsulfide (HEPSI) by Excess Peroxydisulfate at Ambient Temperature (22°C)

phenylsulfide with excess amount of peroxydisulfate (see Figures 3-6 and 3-7). While all of the chloroethyl phenylsulfide was oxidized before the first measurement could be made, a measurable rate was obtained for hydroxyethyl phenylsulfide oxidation. This suggests that peroxydisulfate oxidizes chloroethyl phenylsulfide faster than hydroxyethyl phenylsulfide. No chlorinated reaction products (such as CEPSO) were observed in either the Oxone or peroxydisulfate experiments.

3.2.3.4 Impact of Temperature Elevation on the Degradation of Chloroethyl Phenylsulfide in Aqueous Solution

At elevated temperatures, 60 °C, hydroxyethyl phenylsulfone was again observed to be the predominant reaction product in the presence of both peroxymonosulfate (Oxone) and peroxydisulfate. However, for the Oxone reaction, the formation of hydroxyethyl phenylsulfone is very rapid and it slowly degraded at a rate of 0.018 hr^{-1}, Figure 3-8. The formation of hydroxyethyl phenylsulfone is less rapid for peroxydisulfate oxidation, with the oxidation of hydroxyethyl phenylsulfide observed to be 4.75 hr^{-1}, but the further degradation of the sulfone is relatively rapid at 0.31 hr^{-1}, Figure 3-9. All the known reaction products are nearly gone from solution after 6 hours. It is assumed that the chloroethyl phenylsulfide is mineralized to CO_2, Cl^-, and SO_4^{2-}, but this could not be confirmed because the starting material was not ^{14}C- and ^{35}S-labelled and the observed SO_4^{2-} could not be differentiated from sulfate produced by peroxydisulfate degradation. Ion chromatography detected chloride and a small amount of chlorate in solution.

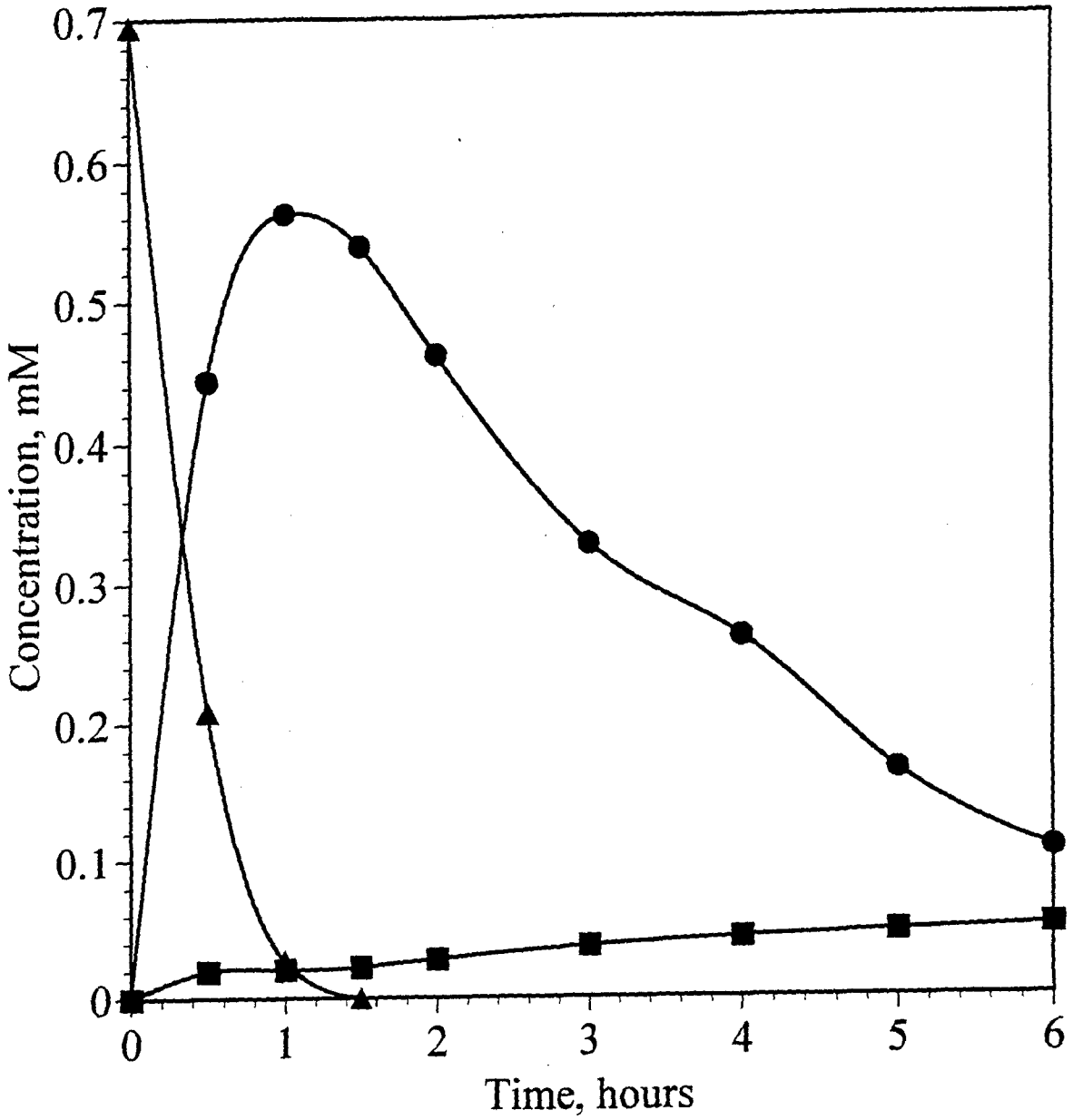
The difference in reactivity observed between the peroxysulfate compounds and at different temperatures was expected. Peroxymonosulfate reacts rapidly with oxidizable substances – especially those containing sulfur species. Peroxydisulfate, on the other hand, has kinetic barriers that prevent rapid oxidation. At elevated temperatures, peroxymonosulfate (Oxone) reactions will increase in rate as expected from the Arrhenius equation. Peroxydisulfate, however, decomposes at high temperature to sulfate radical anions, $SO_4^{\cdot-}$. These radicals are extremely powerful oxidizing agents and do not have



Data represent concentrations of the degradation products hydroxyethyl phenylsulfone (triangles) and hydroxyethyl phenylsulfoxide (circles) at various times after addition of peroxymonosulfate to an aqueous solution of the HD simulant chloroethyl phenylsulfide. The squares represent the simulants' hydrolysis product (hydroxyethyl phenylsulfide) concentrations without added Oxone.

Figure 3-8

Oxidation of the HD Simulant Chloroethyl Phenylsulfide (CEPSI) by Peroxymonosulfate (Oxone) at 60°C



Data represent concentrations of simulants' hydrolysis product hydroxyethyl phenylsulfide (triangles), and the degradation products hydroxyethyl phenylsulfone (circles) and hydroxyethyl phenylsulfoxide (squares) after addition of peroxydisulfate to aqueous solutions containing the HD simulant chloroethyl phenylsulfide.

Figure 3-9

Oxidation of the HD Simulant Chloroethyl Phenylsulfide (CEPSI) by Peroxydisulfate at 60°C

substantial kinetic barriers to oxidations. They oxidize virtually any organic compound. The extent of this behavior can be seen by comparing Figures 3-7 and 3-9. At room temperature, peroxydisulfate converts hydroxyethyl phenylsulfide to hydroxyethyl phenylsulfone at a rate of 0.427 hr^{-1}. At 60 °C hydroxyethyl phenylsulfide is converted to hydroxyethyl phenylsulfone at a rate of 4.77 hr^{-1} and the hydroxyethyl phenylsulfone is further degraded at a rate of 0.31 hr^{-1}. The results are all qualitatively consistent with previous findings.[6]

3.2.4 Peroxymonosulfate (Oxone) Oxidation of the HD Simulant Chloroethyl Phenylsulfide in Slurries Containing Spiked Soil

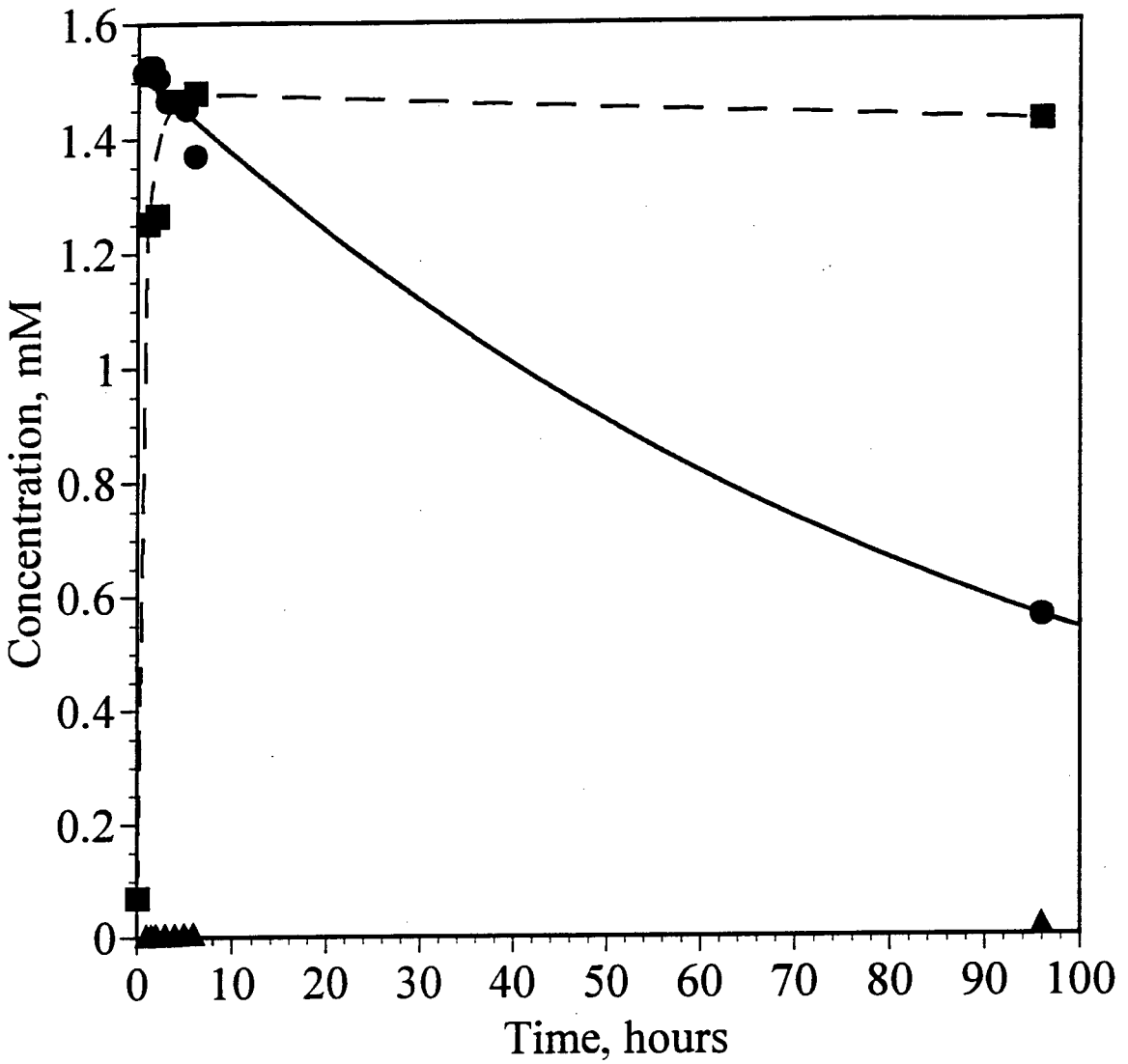
This experiment consisted of two parts, a baseline hydrolysis of the HD simulant in the absence of oxidant and the addition of spiked soil to a slurry containing peroxymonosulfate.

3.2.4.1 Hydrolysis Reactions in Soil Slurries at 60 °C

When 10 g of soil spiked with chloroethyl phenylsulfide (350 ppm) was slurried in 100 mL of water at 60 °C the sole product observed in solution was hydroxyethyl phenylsulfide, and it slowly accumulated in solution over the first ten hours, Figure 3-10. After ten hours, no further increase in hydroxyethyl phenylsulfide concentration occurred, signaling that hydrolysis of the sorbed chloroethyl phenylsulfide was complete.

3.2.4.2 Reaction with Peroxymonosulfate at 60 °C

A second 10 g sample of the same spiked soil was slurried in 100 mL of 3.25 mM peroxymonosulfate (Oxone) solution. Quantitative conversion of the chloroethyl phenylsulfide to chloroethyl phenylsulfone and a negligible amount of phenyl vinylsulfone ($C_6H_5SO_2CHCH_2$) was observed (Figure 3-10). The primary reaction product, chloroethyl



Data represent concentrations of the degradation products chloroethyl phenylsulfone (circles) and phenyl vinylsulfone (triangles) after addition of peroxymonosulfate (Oxone) to an aqueous solution containing soil spiked with the HD simulant chloroethyl phenylsulfide. As a frame of reference, for the case in which peroxymonosulfate is absent, the concentrations of the simulants' hydrolysis product, hydroxyethyl phenylsulfide (squares), are also provided.

Figure 3-10

Oxidation of the HD Simulant Chloroethyl Phenylsulfide (CEPSI) in Slurries Containing Spiked Soil by Peroxymonosulfate at 60°C

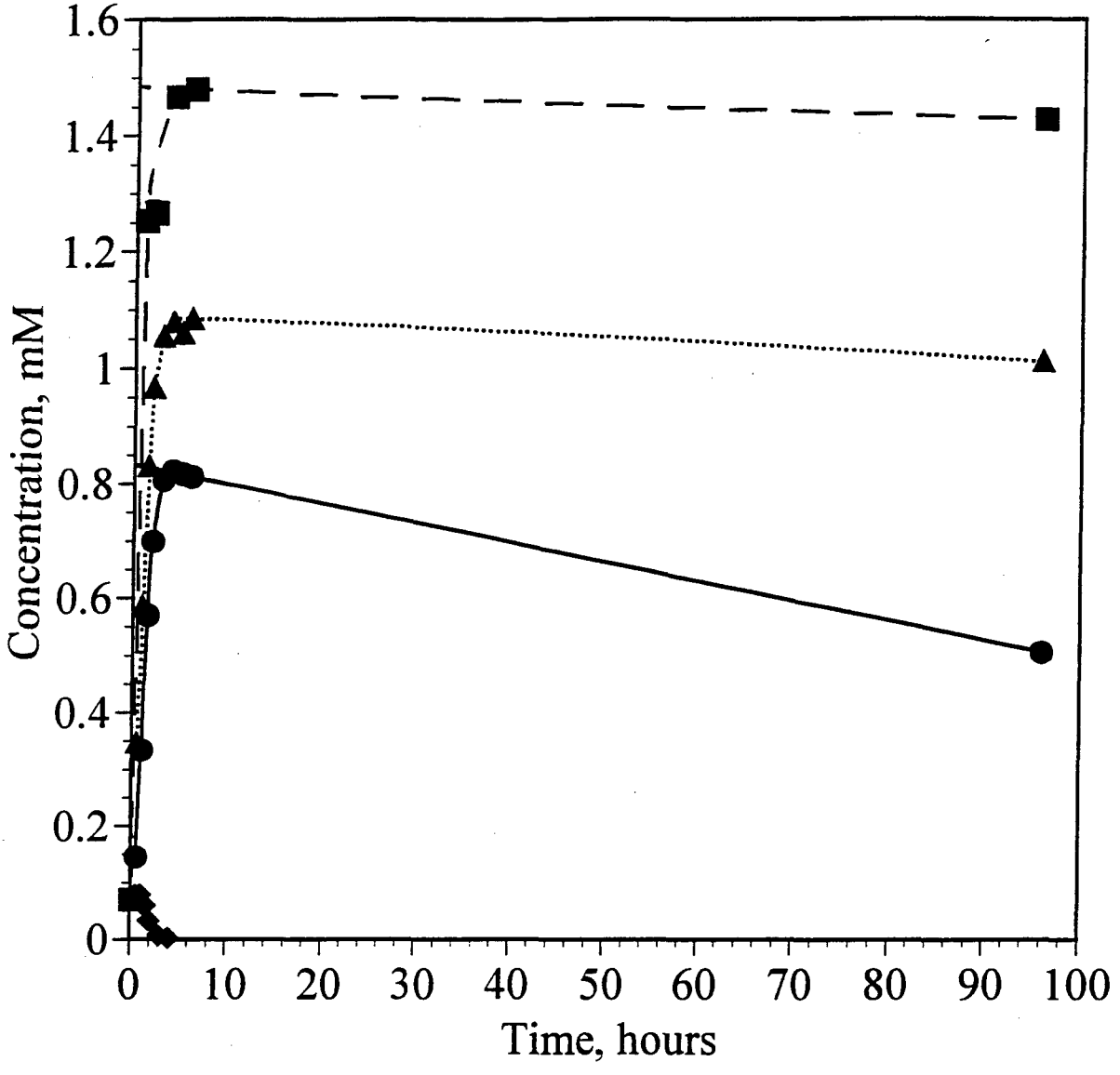
phenylsulfone ($C_6H_5SO_2CH_2CH_2Cl$), is a mild vessicant, but is considered nontoxic. The presence of phenyl vinylsulfone, however, is of concern since it is considered highly toxic. No hydrolysis products were observed in the presence of peroxymonosulfate. The chloroethyl phenylsulfone degraded further at a rate of 0.01 hr^{-1} to unknown products.

3.2.5 Peroxydisulfate Oxidation of Chloroethyl Phenylsulfide in Slurries Containing Spiked Soil

A room temperature (25 °C) soil (10 g) spiked with chloroethyl phenylsulfide (350 ppm) was slurried with 100 mL ammonium peroxydisulfate (1%, 44 mM) solution. Both chloroethyl phenylsulfone and hydroxyethyl phenylsulfone appeared in solution, Figure 3-11.

The chloroethyl phenylsulfone degraded further at a rate of 6.4×10^{-4} hr^{-1}. The hydroxyethyl phenylsulfone degraded at a rate of 5.3×10^{-3} hr^{-1}. The reduced rate of oxidation and the increased pH of the peroxydisulfate solution, relative to solutions of Oxone, allowed some hydrolysis and subsequent oxidation of the hydroxyethyl phenylsulfide to occur. The hydroxyethyl phenylsulfide was found to degrade at a rate of 1.30 hr^{-1}.

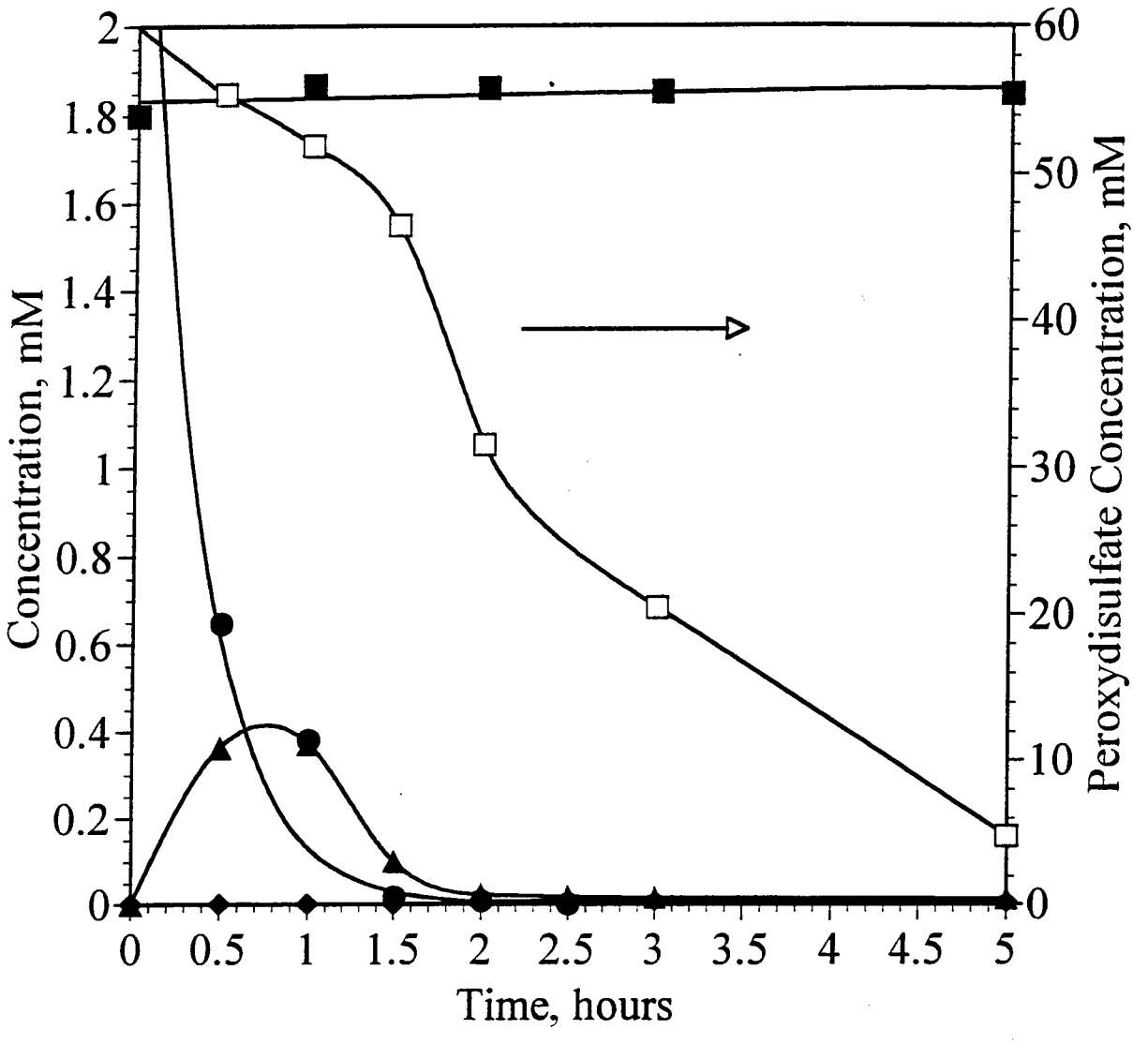
At 75 °C, a 1 percent peroxydisulfate solution rapidly reduced all observable sulfur compounds below their analytical method detection limits (MDL for CEPSI = 0.09 mg/L), Figure 3-12. The degradation of chloroethyl phenylsulfide occurred at a rate of 3.05 hr^{-1}. Some chloroethyl phenylsulfone, and even less phenyl vinylsulfone, accumulated in solution, but were completely degraded before 3 hours. The decrease in $S_2O_8^{2-}$ concentration was monitored by Raman spectroscopy. The initial $S_2O_8^{2-}$ concentration was approximately 30 times the initial chloroethyl phenylsulfide concentration. After 5 hours the $S_2O_8^{2-}$ concentration had been reduced at a rate of 0.56 hr^{-1} to only 2.5 mM.



Data represent the concentrations of chloroethyl phenylsulfone (triangles), hydroxyethyl phenylsulfone (circles), and hydroxyethyl phenylsulfide (diamonds) in solution after the addition of 1 % peroxydisulfate to a chloroethyl phenylsulfide spiked soil. Squares represent hydroxyethyl phenylsulfide concentrations in a solution containing no peroxymonosulfate.

Figure 3-11

Peroxydisulfate oxidation of the HD simulant Chloroethyl Phenylsulfide (CEPSI) in Slurries Containing Spiked Soil at 25°C



Left hand scale: Data represent concentrations of the HD simulant chloroethyl phenylsulfide (dark circles), the degradation products chloroethyl phenylsulfone (dark triangles) and phenyl vinylsulfone (dark diamonds) after addition of peroxydisulfate. As a frame of reference, concentrations the simulants hydrolysis product hydroxyethyl phenylsulfide (dark squares) is also provided (for aqueous solutions containing chloroethyl phenylsulfide but no peroxydisulfate).

Right hand scale: Peroxydisulfate concentration (open squares) showing degradation with time.

Figure 3-12

Peroxydisulfate oxidation of the HD Simulant Chloroethyl Phenylsulfide (CEPSI) in Slurries Containing Spiked Soil at 75°C

3.3 Degradation of GB Simulants

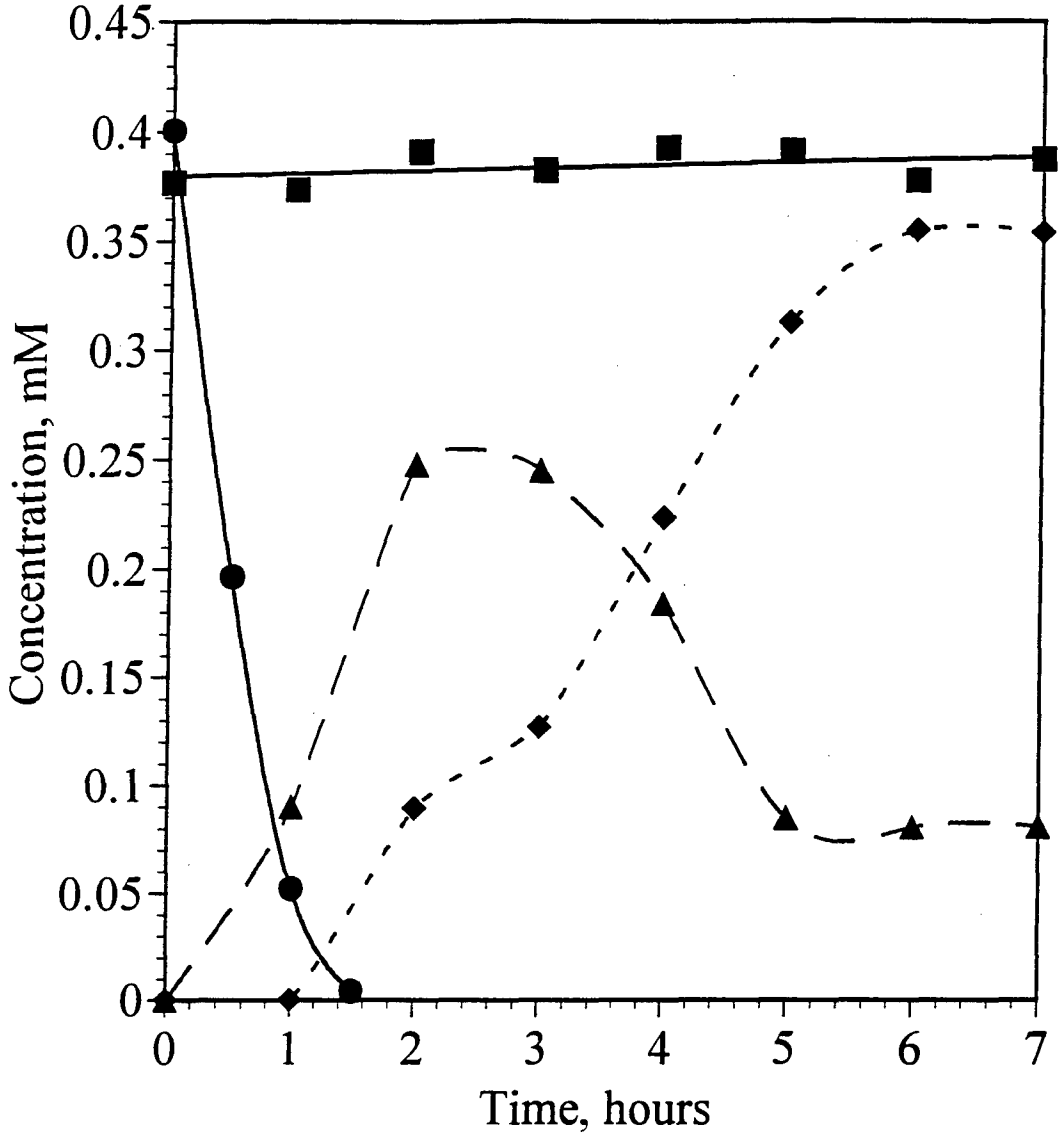
3.3.1 Hydrolysis of the GB Simulant Diisopropyl Methylphosphonate

In the absence of oxidants, solutions of 100 ppm diisopropyl methylphosphonate ($CH_3PO[(OCH(CH_3)_2]_2$) remained stable over the seven hour time frame of the experiments and no hydrolysis was observed. Solution pH (2 to 7) and temperature (25 to 90 °C) had no effect on hydrolysis or volatilization rates. In the presence of peroxysulfates, any observed decrease in diisopropyl methylphosphonate concentration, or the appearance of methylphosphonic acid and phosphate, could be attributed solely to oxidation.

3.3.2 Oxidation of the GB Simulant Diisopropyl Methylphosphonate by Peroxysulfates in Aqueous Solution

At room temperature no reaction between diisopropyl methylphosphonate (100 ppm or 0.5 mM) and peroxydisulfate (20 mM $Na_2S_2O_8$) or peroxymonosulfate (3 mM HSO_5^-) was observed within the seven hour experimental time frame used for all the DIMP oxidation experiments. Neither peroxymonosulfate nor peroxydisulfate was a strong enough oxidant to attack diisopropyl methylphosphonate.

At elevated temperatures peroxydisulfate decomposed into sulfate radical anions which were capable of degrading diisopropyl methylphosphonate. In a 20 mM peroxydisulfate solution at 60 °C, the diisopropyl methylphosphonate was degraded at a rate of 2.97 hr^{-1}, Figure 3-13. Methylphosphonic acid ($CH_3PO(OH)_2$), produced by the diisopropyl methylphosphonate degradation, accumulated in solution and then decreased in concentration as phosphate was observed to be formed. After 6 hours some residual methylphosphonic acid remained, but nearly all of the diisopropyl methylphosphonate had been completely mineralized to phosphate.



Data represent concentrations of GB simulant diisopropyl methylphosphonate (circles), and the degradation products methylphosphonic acid (triangles) and phosphate (diamonds) in a 20 mM aqueous peroxydisulfate solution. Data for diisopropyl methylphosphonate (squares) in the absence of peroxydisulfate is also shown.

Figure 3-13

Peroxydisulfate Oxidation of the GB Simulant Diisopropyl Methylphosphonate (DIMP) in Aqueous Solutions at 60°C

3.3.3 Oxidation of the GB Simulant Diisopropyl Methylphosphonate by Peroxydisulfate in Slurries Containing Spiked Soil

A 15 mM peroxydisulfate solution was heated to 90 °C and a 1000 ppm diisopropyl methylphosphonate spiked soil was added. The mixture was 90 percent water and 10 percent soil.

The GB simulant, Diisopropyl methylphosphonate, was reduced to concentrations below the analytical method's detection limit for DIMP (0.048 mg/L) after one hour, Figure 3-14. In addition, degradation products, specifically methylphosphonic acid ($CH_3PO(OH)_2$) and phosphates, were observed to accumulate in solution.

However, unlike the experiment with aqueous solutions, there was no induction period before the phosphate was observed. Furthermore, the methylphosphonic acid reached a steady state concentration and did not continue degrading, Figure 3-14. The final concentration of the methylphosphonic acid was roughly equal to the initial concentration of the diisopropyl methylphosphonate. The initial concentration of diisopropyl methylphosphonate was not sufficient to account for the amounts of methylphosphonic acid and phosphate observed after oxidation.

It currently appears that soil borne phosphorus was converted into a water soluble phosphate form. An unspiked soil subjected to the same peroxydisulfate treatment produced nearly the same amount of phosphate in solution; while an unspiked soil in deionized water containing no added oxidant produced no phosphate. Elemental analysis of the soil showed the phosphorus content to be 0.2 %, so the soil contained more than enough phosphorus to account for the observed phosphate.

The methylphosphonic acid did show signs of degrading after several hours (Figure 3-14), and experiments performed in the absence of soil (see section 3.3.2) demonstrated that

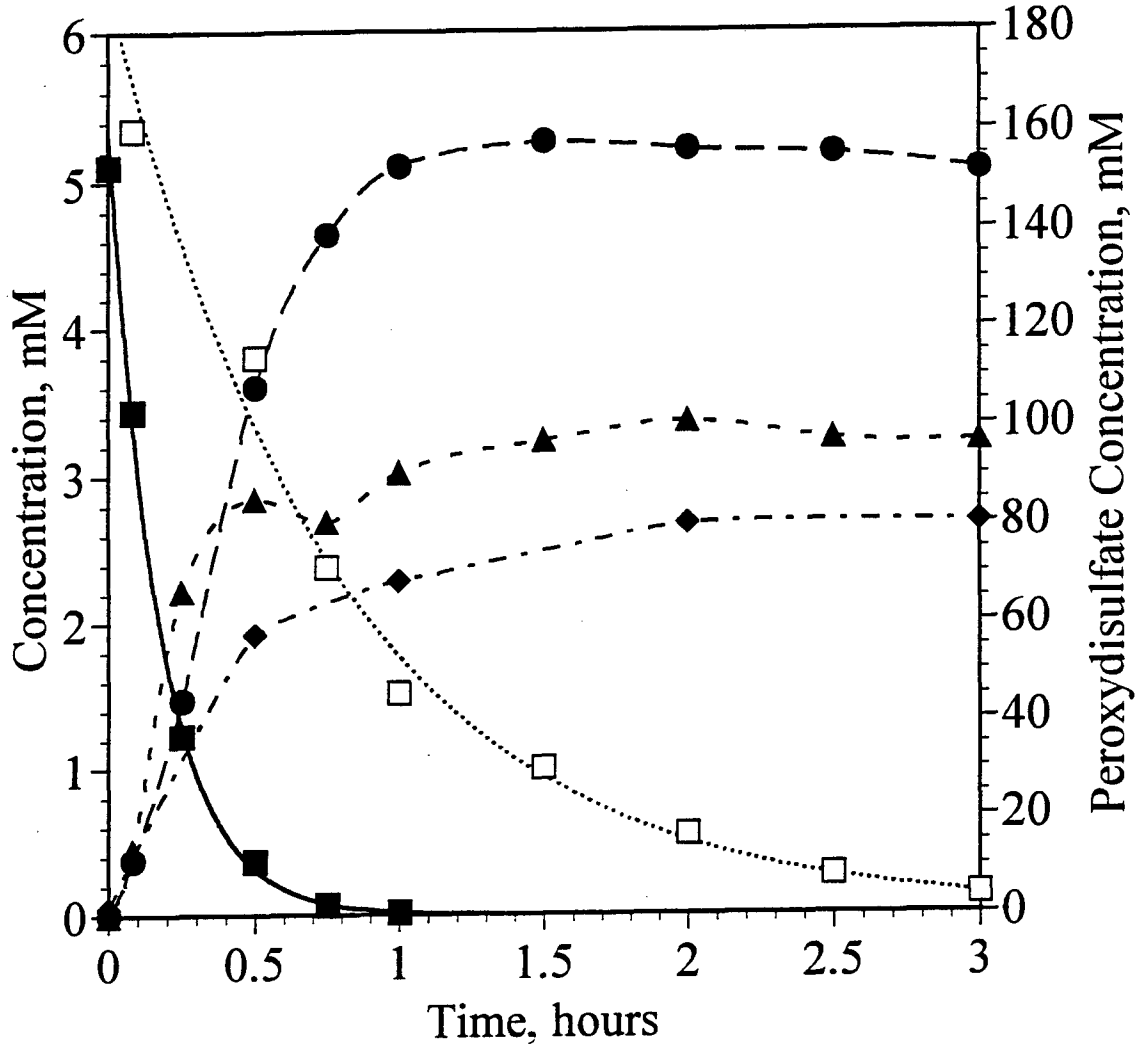
peroxydisulfate can oxidize methylphosphonic acid to phosphate. The slow rate of methylphosphonic acid degradation in soil implies that there is substantial competition from the soil and large amounts of oxidative equivalents are consumed by competitive reactions. The source of the phosphate could not be conclusively determined because phosphate formed from methylphosphonic acid degradation could not be distinguished from phosphate produced in soil reactions.

The rate of peroxydisulfate degradation was 1.07 hr^{-1} in the presence of diisopropyl methylphosphonate spiked soil, see right hand Y-axis of Figure 3-14. The half life of peroxydisulfate was 38 minutes, consistent with the rate of $S_2O_8^{2-}$ degradation in the presence of the same soil before spiking (see Section 3.1). Since the rate determining step for peroxydisulfate decomposition is O-O bond cleavage, equation 9, no rate enhancement from diisopropyl methylphosphonate was expected. The diisopropyl methylphosphonate (R in equation 10) is oxidized by $SO_4^{\cdot-}$ generated by O-O bond cleavage, not direct oxidation by $S_2O_8^{2-}$, so diisopropyl methylphosphonate does not contribute directly to the degradation of $S_2O_8^{2-}$.

$$S_2O_8^{2-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\ SO_4^{\cdot-} \qquad (9)$$

$$SO_4^{\cdot-} + R \xrightarrow{k_2} SO_4^{2-} + O \quad (R = \text{reductant, } O = \text{oxidant}) \qquad (10)$$

The rate of $SO_4^{\cdot-}$ dimerization, k_{-1}, and diisopropyl methylphosphonate oxidation, k_2, are both nearly diffusion controlled.[7] Under these conditions the overall reaction rate for $S_2O_8^{2-}$ degradation is determined by the rate of O-O bond cleavage, k_1.[8] This rate should apply universally for all peroxydisulfate oxidations unless the species being oxidized, R, in equation 10 can react directly with $S_2O_8^{2-}$ as was the case for the HD simulant chloroethyl phenylsulfide, equation 7.



Left hand scale: Data represent the concentrations of the GB simulant diisopropyl methylphosphonate (dark squares), the degradation products methylphosphonic acid (dark circles) and phosphate (dark triangles), in a 10 % soil slurry in 150 mM aqueous peroxydisulfate. Phosphate concentrations in an unspiked soil slurried in peroxydisulfate solution (dark diamonds) are also shown.

Right hand scale: Peroxydisulfate concentrations (open squares) show degradation of the oxidant with time.

Figure 3-14

Peroxydisulfate Oxidation of the GB Simulant Diisopropyl Methylphosphonate (DIMP) in Slurries Containing Spiked Soil at 90°C

Increased rates of GB simulant degradation were achieved by increasing the concentration of peroxydisulfate used, Figure 3-15. In the 150 mM peroxydisulfate solution above, the GB simulant (diisopropyl methylphosphonate) degraded at a rate of 5.72 hr^{-1} and was reduced below detection limits after one hour. Other tests conducted with soil slurries at 90 °C indicated that the diisopropyl methylphosphonate degraded at a rate of 0.12 hr^{-1} in 1% (37 mM) peroxydisulfate solution, 1.19 hr^{-1} in 2% (74 mM) solution, and 15.5 hr^{-1} in 3.8% (140 mM) solution.

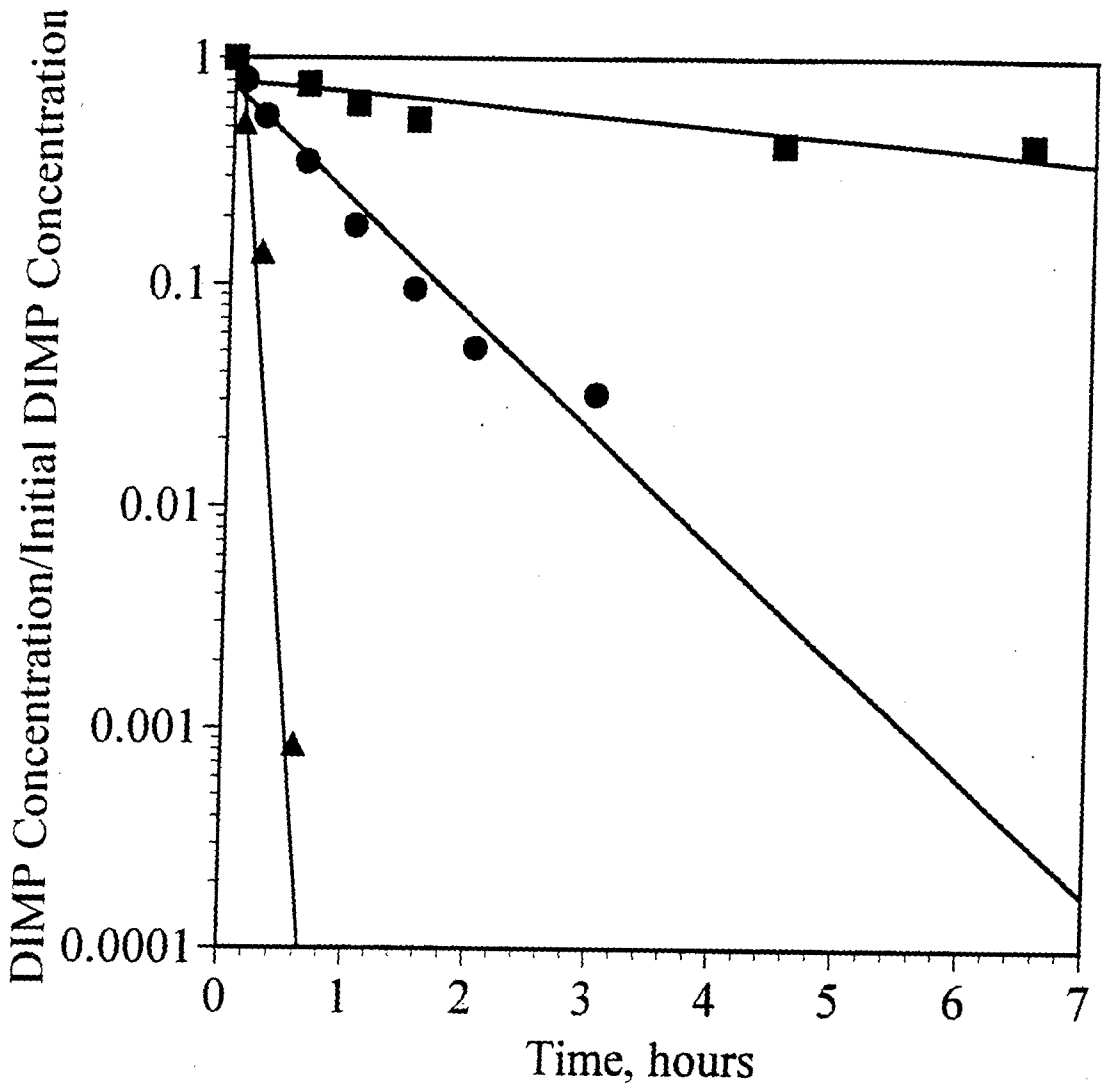
3.4 Degradation of VX Simulants

3.4.1 Hydrolysis of the VX Simulant O-ethyl S-ethyl Phenylphosphonothioate

A 10 mM aqueous solution of O-ethyl S-ethyl phenylphosphonothioate (OSDEPPT) in 100 mM NaOH underwent hydrolysis. The OSDEPPT disappeared from solution at a pseudo first order rate of 0.03 min^{-1}, Fig. 3-16. The observed half life of 23 minutes was consistent with previously reported $t_{1/2}$ of 18 minutes.[9]

3.4.2 Oxidation of the VX Simulant O-ethyl S-ethyl Phenylphosphonothioate by Peroxymonosulfate (Oxone) in Aqueous Solution at 25 °C

Oxone (50 mM peroxymonosulfate) was added to a 5 mM aqueous solution of OSDEPPT. The room temperature (25 °C) rate of degradation of the OSDEPPT was observed to be 0.14 min^{-1}, Fig. 3-17. The OSDEPPT concentration was reduced below the analytical method's detection limit (0.0063 mg/L) in less than one hour. The solution pH was 2.8 and oxidation occurred at substantially higher rate than hydrolysis. The peroxymonosulfate degraded very slowly and the rate did not appear to be first order.



Data represent concentrations of the GB simulant diisopropyl methylphosphonate in peroxydisulfate solution concentrations of 1 % (squares), 2 % (circles), and 3.8 % (triangles) by weight.

Figure 3-15

Variations of the GB Simulant Degradation Rate with Peroxydisulfate Concentration in Slurries Containing Spiked Soil at 90°C

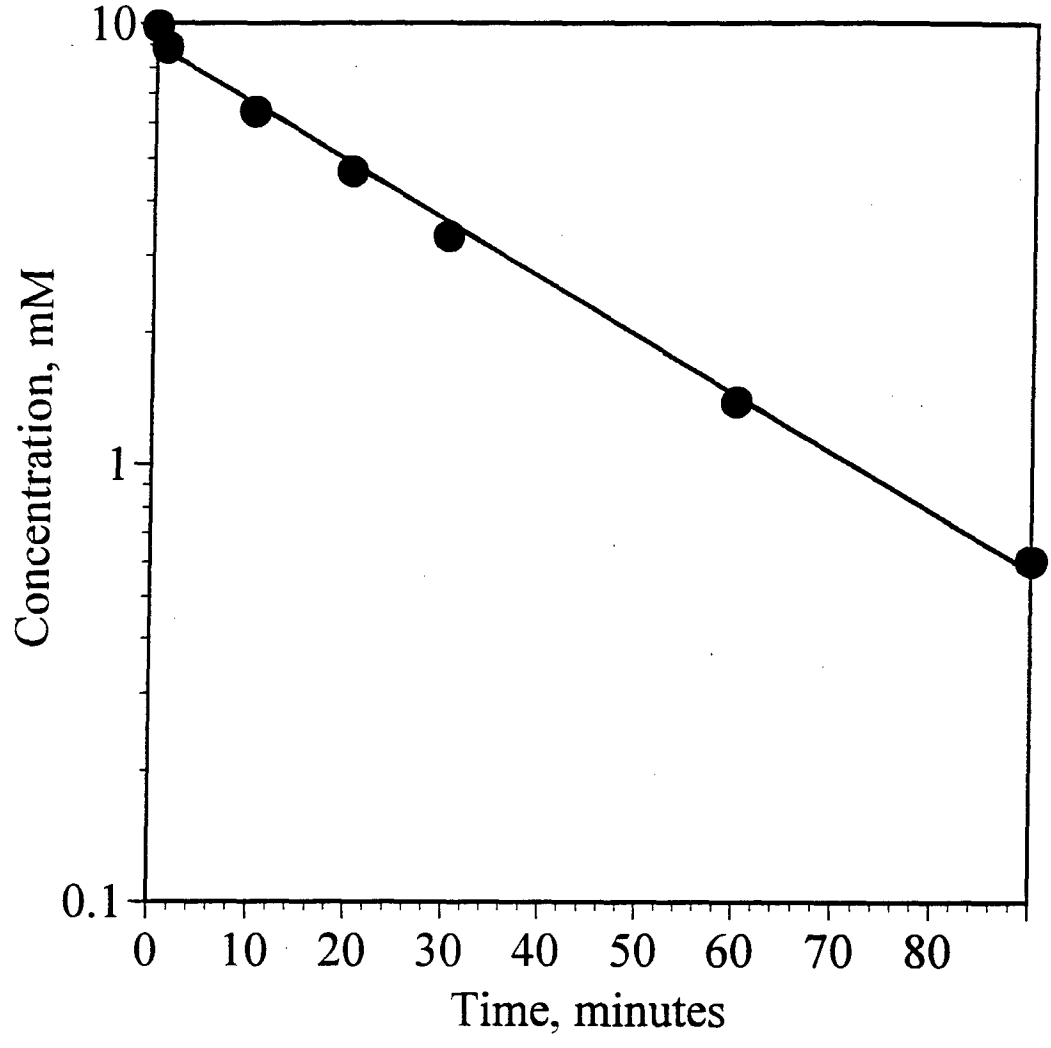
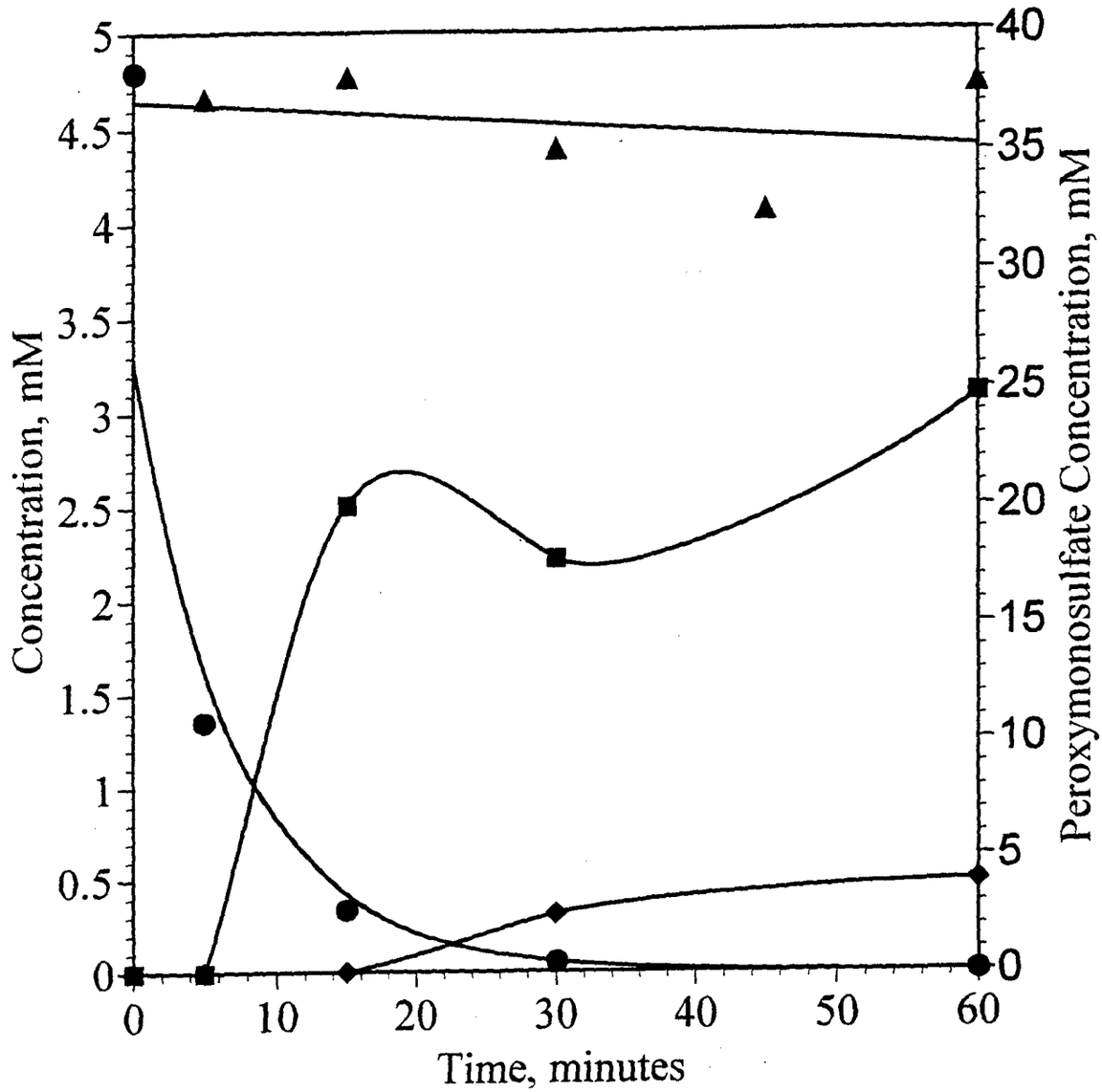


Figure 3-16

Hydrolysis of the VX simulant O-ethyl S-ethyl phenylphosphonothioate (OSDEPPT) in 100 mM NaOH Solution



Data represent concentrations of the VX simulant O-ethyl S-ethyl Phenylphosphonothioate (circles), O-ethyl phenylphosphonate (squares), phosphate (diamonds), and peroxymonosulfate (triangles).

Figure 3-17

Peroxymonosulfate (Oxone) Oxidation of the VX Simulant O-ethyl S-ethyl Phenylphosphonothioate (OSDEPPT) at 25 °C

3.4.3 Oxidation of the VX Simulant O-ethyl S-ethyl Phenylphosphonothioate by Peroxydisulfate in Aqueous Solutions at 25 and 90 °C

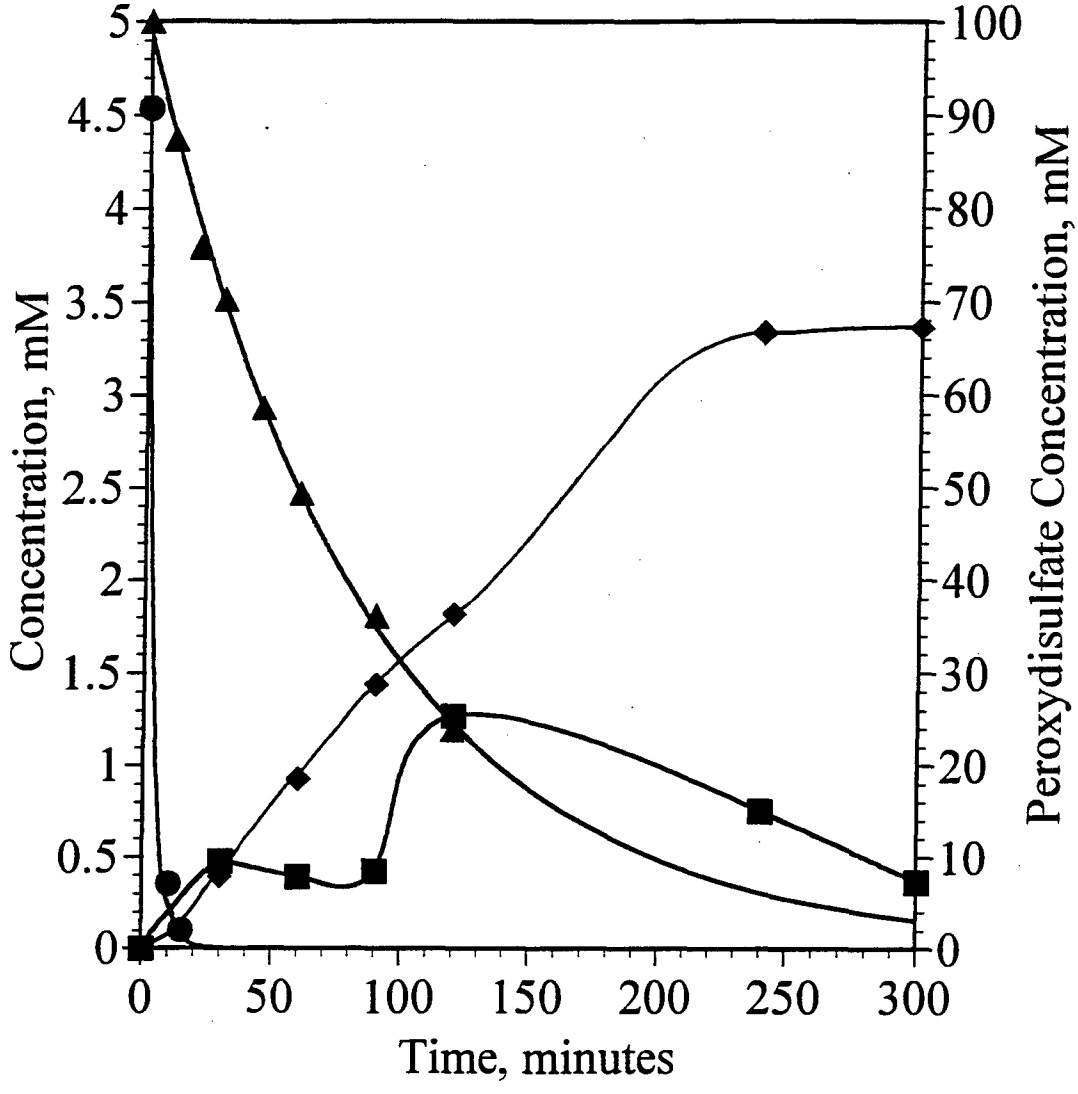
Potassium peroxydisulfate (100 mM) was added to aqueous solutions of 5 mM OSDEPPT. At room temperature no appreciable degradation of the OSDEPPT occurred over a 5-hour time frame. At 90 °C the OSDEPPT degraded at a rate of 0.25 min^{-1}, Fig. 3-18. Within 30 minutes the OSDEPPT concentration was reduced below the analytical method's detection limit for OSDEPPT (0.0063 mg/L). Phosphate was observed to accumulate in solution and accounted for 75% of the starting OSDEPPT after four hours. The peroxydisulfate degraded at a rate of 0.54 hr^{-1}.

3.4.4 Oxidation of the VX Simulant O-ethyl S-ethyl Phenylphosphonothioate (OSDEPPT) by Peroxymonosulfate (Oxone) in Slurries Containing Spiked Soil at 25 °C

A soil spiked with OSDEPPT was slurried in a room temperature 100 mM peroxymonosulfate solution. The OSDEPPT concentration on the soil was 1150 ppm and the slurry contained 10% soil. The OSDEPPT degraded at a rate of 0.23 min^{-1} to concentrations below detection limits within one hour, Fig. 3-19. The Oxone degraded at a rate of 0.80 hr^{-1}.

3.4.5 Oxidation of the VX Simulant O-ethyl S-ethyl Phenylphosphonothioate by Peroxydisulfate in Slurries Containing Soil at 90 °C

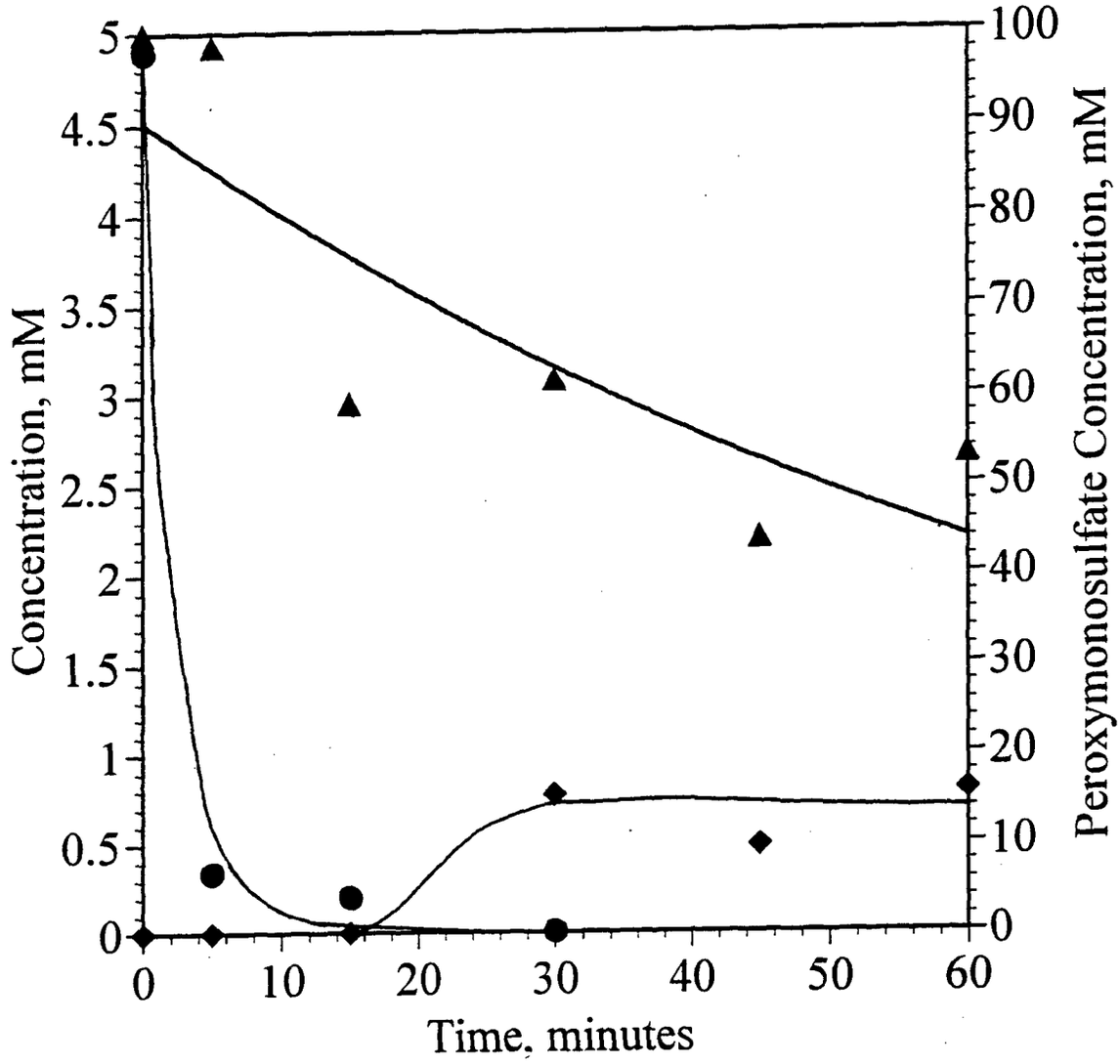
A soil spiked with OSDEPPT was slurried in a 90 °C 100 mM $K_2S_2O_8$ solution. The OSDEPPT concentration on the soil was 1150 ppm and the slurry contained 10% soil. The OSDEPPT degraded at a rate of 0.25 min^{-1}, Fig. 3-20. The concentration of OSDEPPT was reduced below detection limits within 30 minutes reaction time. Phosphate was observed to accumulate in solution. As in the case of the GB simulant,



Data represent concentrations of VX simulant O-ethyl S-ethyl Phenylphosphonothioate (circles), the degradation products O-ethyl phenylphosphonate (squares) and phosphate (diamonds), and the oxidant peroxydisulfate (triangles).

Figure 3-18

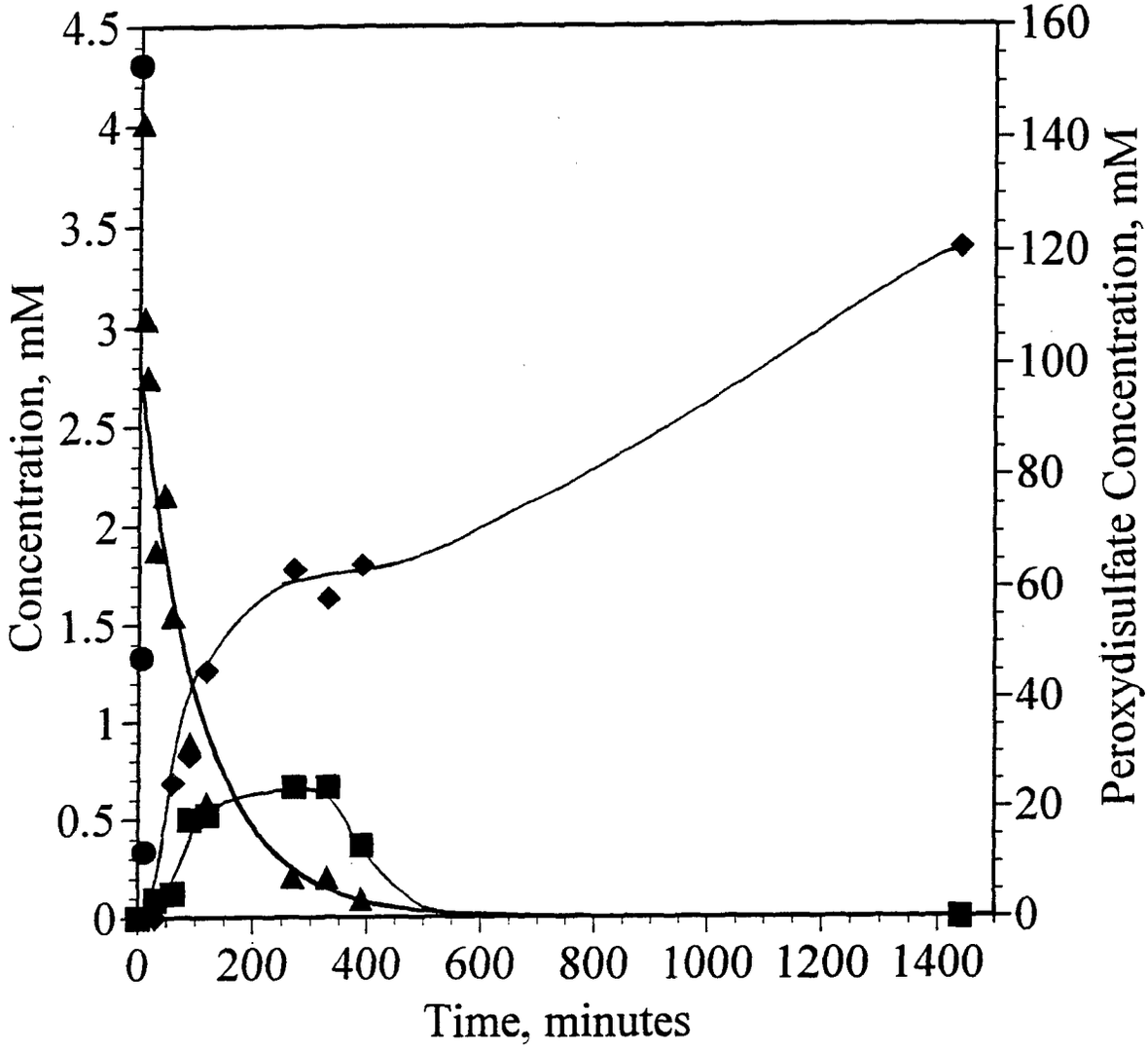
Peroxydisulfate Oxidation of the VX Simulant O-ethyl S-ethyl Phenylphosphonothioate (OSDEPPT) at 90 °C



Data represent concentrations of the VX simulant O-ethyl S-ethyl Phenylphosphonothioate (circles), the degradation product phosphate (diamonds), and the oxidant peroxymonosulfate (triangles).

Figure 3-19

Peroxymonosulfate (Oxone) Oxidation of the VX simulant O-ethyl S-ethyl Phenylphosphonothioate (OSDEPPT) in Slurries Containing Spiked Soil at 25°C



Data represent concentrations of the VX simulant O-ethyl S-ethyl phenylphosphonothioate (circles), the degradation products O-ethyl phenylphosphonate (squares) and phosphate (diamonds), and the oxidant peroxydisulfate (triangles).

Figure 3-20

Peroxydisulfate Oxidation of the VX simulant O-ethyl S-ethyl Phenylphosphonothioate (OSDEPPT) in Slurries Containing Spiked Soil at 90°C

diisopropyl methylphosphonate, phosphate was also observed in a blank sample of clean, unspiked soil slurried in 90 °C 100 mM $K_2S_2O_8$ solution. A rough estimate of the concentration of phosphate arising from OSDEPPT mineralization was made by subtracting the phosphate concentration found after the oxidation of unspiked soil from the phosphate concentration in the oxidized OSDEPPT spiked soil. After four hours, the phosphate accounted for 61% of the starting OSDEPPT concentration. The peroxydisulfate degraded at a rate of 0.70 hr^{-1}. The OSDEPPT degraded at a constant rate in solution and in soils, and evidence for mineralization was obtained in both solution and soil. The competition for oxidative equivalents by the soil does not appear to be as severe as in the case of DIMP.

3.5 Conceptual Design

3.5.1 Introduction

The conceptual design described below is for a small batch demonstration plant capable of treating soils contaminated with chemical warfare agents such as GB, HD, or VX. The plant is designed for demonstrating the mineralization of chemical warfare agents with peroxysulfates. However, the plant is transportable and can be used for small-scale soil treatment. For design purposes, the plant was sized to process up to 750 pounds (340 Kg) of soil per eight hour shift. This is slightly more than the amount of soil that would fill a 55 gallon drum. The design includes a conceptual cost estimate for construction of the plant as envisioned.

3.5.2 Process Description

Operating System

The batch plant consists of two units: a soils processing unit and a soils treatment unit, Figure 3-21. The soils processing unit (see upper left hand corner of Figure 3-21) consists of:

- A pug mill for breaking-up clods and ensuring the soil will flow though downstream operations.
- An elevator for lifting soil from the pug mill to a hopper.
- A surge hopper for storing soil processed by the pug mill.
- A screw conveyor for moving soil between the hopper and a ball mill.
- A batch type wet ball mill for grinding any rocks to approximately -35 mesh.
- And a slurry pump for pumping the ground slurry to the soils treatment unit.

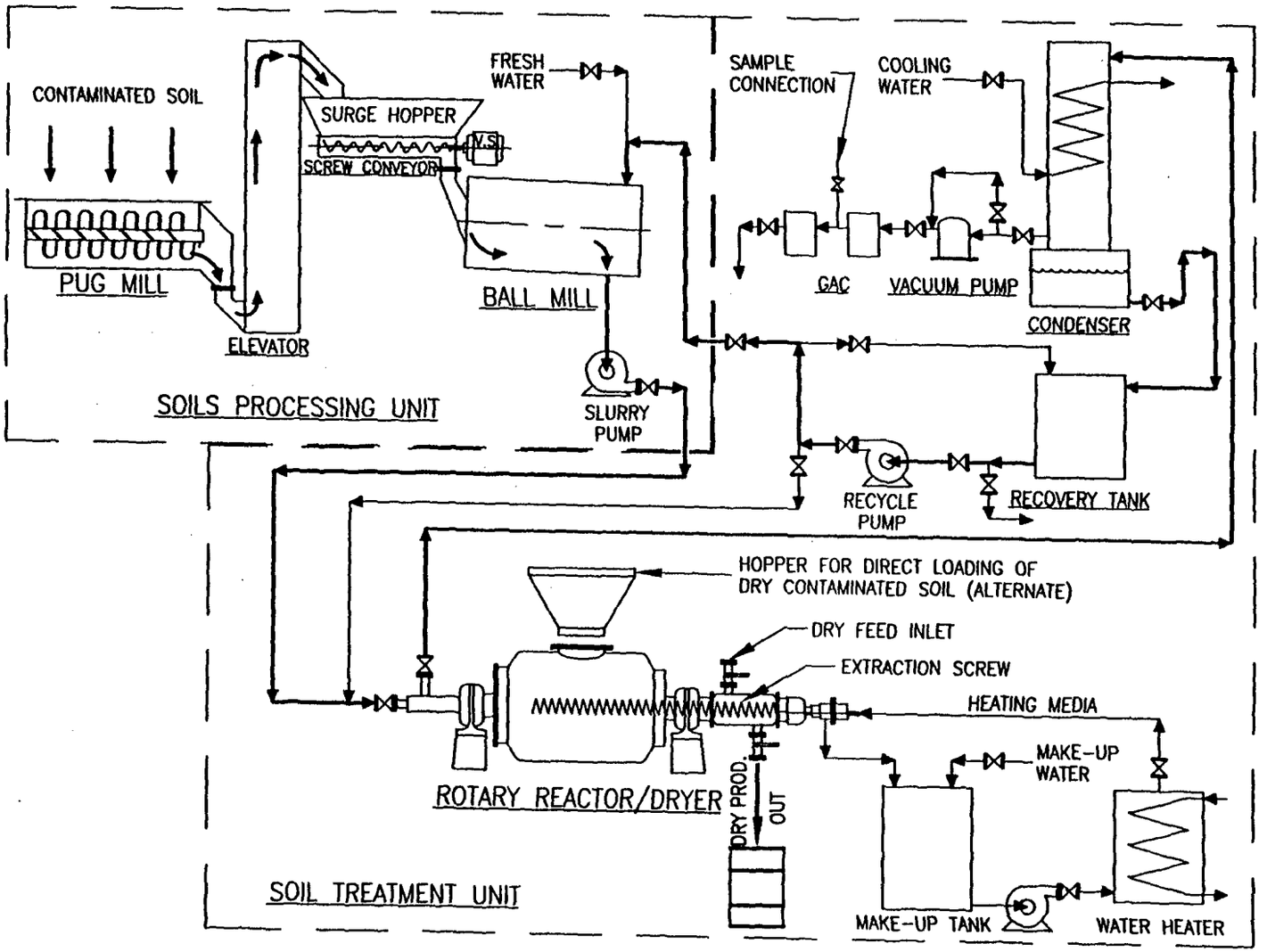


Figure 3-21

Flow Diagram for Peroxysulfate Pilot Plant

The soil processing unit has been designed with operational flexibility in mind and can be operated in one of two modes. In the first mode, soil is transformed into a slurry. In this mode, the contaminated soil is loaded, either manually or by a front end loader, into the pug mill. Here any large clods are crushed. The soil then flows into a bucket elevator and rises to a height of ten feet before being deposited into a covered 10 cubic foot surge hopper. To reduce the potential for dust production, the bucket elevator is operated just fast enough to keep up with the discharge from the pug mill. From the hopper, the contaminated soil flows into a batch type ball mill via a screw conveyor. Once the ball mill is loaded with soil; water, recycled from the soil treatment plant, is added to the mill until the mixture is 30-65% solids. The mixture is ground until the soils particle size is reduced to 95% minus 35 mesh. The slurry is then emptied into a slurry pump and flows to the soil treatment unit via a 1-inch stainless steel line.

In the second operating mode, the soil is simply rendered free flowing and loaded into a Roura hopper (a moveable product bin). The flow of materials is the same as in the first mode except the ball mill is by-passed at the screw conveyor and the soil flows into a product bin instead. This mode was designed to allow for the processing of soils found to be too difficult to slurry or grind -- heavy clays for example. The filled Roura hopper is covered and shipped to the soil treatment unit via forklift.

The soil treatment unit (right half of Figure 3-21) consists of:

- A rotary reactor/dryer.
- A heating media system for circulating hot water through the rotary reactor/dryer's jacket.
- A vacuum based condensing system for recovering water vapor from the rotary reactor/dryer.

- A carbon based filter for removing residual agent from gases leaving the condensing system for discharge to the atmosphere.

The rotary reactor/dryer is hereafter referred to as the "reactor."

The soil treatment unit can be operated in two modes. In the first mode the reactor can be loaded via the 1 inch slurry line. In the second mode the reactor is loaded manually with soil.

Process operations in the first operating mode are as follows. First the reactor is loaded with peroxysulfate in one of three ways (Figure 3-21):

- Direct manual loading via an access hatch on the side of the reactor. Access to the hatch is via a hole in the floor of a platform located above the reactor.

- Pumping a premixed peroxysulfate solution into the reactor via the feed line.

- Indirect manual loading of solids. The solids enter through the dry feed inlet and flow into the reactor chamber by reversing the direction of the reactors' extraction screw (reverse rotation of the screw).

Direct manual loading is the preferred method.

Once the peroxysulfate has been loaded, the reactor hatch is sealed and the slurry containing the contaminated soil is pumped into the reactor from the ball mill. The reactor consists of a jacketed drum containing steel balls that circulate, with the soil, along the horizontal axis. Drum rotation begins prior to loading the slurry and right after the peroxysulfate is loaded. The steel balls prevent mud from sticking to the sides of the reactor walls. If grinding is required, a larger ball charge can be added. Likewise, the

steel balls can be removed if grinding is considered undesirable and the wet soil is unlikely to adhere to the sides of the vessel.

Treatment of the soil begins when: the jacketed reactor is heated to a temperature of 90 °C (194 °F) using heated water from the heating media system (see lower right hand corner of Figure 3-21); the line between the ball mill and reactor is closed; the line between the reactor and the condensing system is opened; and the vacuum pump is bypassed (the pressure in the reactor is kept near atmospheric). During treatment, the reaction vessel's temperature is maintained at 90 °C for three hours – during which the peroxysulfate degrade the chemical warfare agent. The vessel is insulated both to minimize heat loss and for personnel protection.

The heating media system consists of a 30 kW heater, circulation pump, and 100 gallon make-up tank. Water for the heating system is pumped from the make-up tank to the water heater where it is heated to 121 °C (250 °F). The water then flows through the jacketed reactor and back to the make-up tank. All related process lines are insulated.

The condensing system consists of a condenser, vacuum pump, recovery tank, and recycle pump (see upper right hand portion of Figure 3-21). When operating the rotary reactor/dryer as a reactor, water vapor from the reactor flows to the water cooled condenser, where it is condensed, and then flows back into the reactor. Non-condensable gases, produced by the mineralization of organic compounds, flow through the condenser and vacuum pump and into a carbon filter -- which removes any traces of chemical agent in the gas prior to discharge to the atmosphere. When operating the reactor as a dryer, the condensed water flows into the recovery tank and is later pumped to the ball mill (i.e., is recycled). The non-condensable gases are, again, discharged through the carbon filter.

The carbon filter is designed to remove any trace of chemical warfare agents from the gases being discharged from the reactor. The carbon filter is a dual filter design. Between the first and second filters, a sample port exists to monitor for the presence of chemical agent in the gases leaving the first filter. A MINICAMS (Miniature Chemical Agent Monitoring System) would be used to detect this presence. Should agent break through the first filter, then the agent would be detected by the MINICAMS and the soil treatment unit would be shut-down. The filters would then be replaced and the system restarted.

The soil will be neutralized and dried, after the mineralization of the agent is complete. Neutralization consists of adding a predetermined amount of calcium hydroxide to the reactor via the dry feed inlet. Drying begins when the isolation valves around the vacuum pump are opened, the vacuum pump is started, and the vacuum pump's by-pass valve is closed. At this point, the pressure in the reactor drops to about 50 mm mercury. The water within the reactor evaporates as it is heated at low pressure. During the drying process, the reaction vessel's temperature is maintained at approximately 38 °C (100 °F) for two hours during which time the soil will be dried to a "moist" semi-solid condition. The temperature in the reactor/dryer is determined by the boiling point of water at that pressure. An additional two to four hours of drying time will be required to return the soil's moisture level to that of the original soil. For design purposes, the entire treatment process is expected to take about eight hours as allocated below:

- Three hours for agent degradation.
- Five hours for drying.

The rate of evaporation may be accelerated by reducing the vacuum pressure to 23 mm mercury -- producing a boiling point of 24 °C (75 °F). However, effective operation of the water cooled condenser becomes problematic at lower pressure due to boiling point limitations. The optimum operating pressure at a given site will depend upon the temperature of the cooling water available.

Once the soil is dry, a soil sample is obtained through the reactor hatch and tested to verify decontamination and proper pH adjustment. Once verification has been received, the soil is discharged from the reaction vessel, via an extraction screw, and flows into either a 55 gallon drum or Roura hopper. The drum is then moved to a temporary storage area prior to being disposed of or returned to the excavation site.

Decontamination System

Decontamination of the plant will be relatively simple. First, all excess solids in the pug mill, elevator, surge hopper, and screw conveyor will be conveyed to the ball mill for grinding and pumped to the soils treatment unit for decontamination.

Next, bleach or peroxysulfate solution would be added to the recovery tank in the condenser section of the soil treatment unit and circulated for about an hour through the ball mill, slurry pump, and recovery tank. This will degrade any contaminates in the interior of these lines. Next, additional peroxysulfate will be added to the reactor and all water from the recovery tank and ball mill will be pumped into the reactor. The reactor will then be operated at elevated temperature to ensure the degradation of any remaining agent. At the end of the treatment process, the water will either be:

- Evaporated and allowed to discharge to the atmosphere.
- Condensed and discharged.
- Or condensed and disposed of as if it was a hazardous material.

Any residue solids would be extracted from the reactor for disposal. Finally, all of the soil handling equipment (pug mill, elevator, surge hopper, and screw conveyor) would be decontaminated by washing the equipment's outer surfaces with bleach, caustic, or peroxysulfate solutions as appropriate.

3.5.3 Operating Philosophy

The conceptual plant described above was designed primarily to demonstrate the mineralization of agent contaminated soils under field conditions – a commercial unit may be designed differently. To operate the demonstration plant, it was envisioned that the soils processing unit should be isolated from the soil treatment unit to:

- Maximize worker safety.
- Minimize the possibility of contaminating clean soil via dust emissions from the soils processing unit.
- Minimize decontamination of the processing equipment upon completion of the project.

Hence, the plant is envisioned to be operated under conditions in which the soil processing unit is housed in a sealed structure in which soil excavation is occurring. The soil treatment unit will be operated in a similar structure some distance from the excavation. The movement of contaminated soils between these units would occur via a pipeline between these structures. The sealed structures in question could consist of air supported vinyl tents -- like those used to cover excavations at other soil contaminated sites. The design of containment structures was considered beyond the scope of the current design; since, a specific site has not been selected and the regulations surrounding the design of such structures vary from state to state.

Open air operation, if allowed by the regulatory agencies, is also possible. In this instance the concept of separating the soil processing and treatment units will continue

to enhance worker safety by permitting the separated units to be positioned parallel to the prevailing winds. The most likely source of emission would be fugitive dust emissions from the soils processing unit. Potential dust emissions will be minimized by wetting the soil during excavation. Excavation of feedstock is envisioned to occur via the use of conventional excavation equipment (hand-held equipment, bull dozer, front end loader, dump truck, etc.).

In the interest of maximizing worker safety, the demonstration plant would be operated by personnel in level A protective equipment with local monitoring whether containment structures are used or not. Level A protection represents the highest level of protection offered and is expected to be necessary for all tasks involving excavation and soil processing. Use of Level A protection for operations involving the soils treatment unit may be somewhat excessive, but, is considered a prudent safeguard against potential equipment failure during the treatment process.

In all cases, operations likely to involve dust production would be done remotely. For example, after loading the pug mill with fresh soil, workers would remove themselves from the immediate area prior to turning on the pug mill and elevator. Likewise workers removing the treated soil from the rotary reactor/dryer would remove themselves from the area prior to turning on the extraction screw. The amount of dust likely to be produced is low due to the prior wetting of the soil. However, remote operation is considered a prudent safeguard until such time as actual dust levels can be measured. The presence of airborne chemical warfare agent during these operations would be monitored from a site remote from both operating units using MINICAMS. Identification of air monitoring sites was not considered within the scope of this design since monitoring location would depend upon a detailed assessment of process vulnerabilities.

3.5.4 Design Objectives

The mission statement for the design of the demonstration plant was "Develop a conceptual design for a demonstration scale plant capable of treating soils contaminated with chemical warfare agents with solutions of peroxysulfate." Within the confines of this mission, seven primary objectives were identified. In order of importance these objectives were:

- Minimize community and worker exposure to agent.
- Demonstrate the essential functions of a commercial embodiment.
- Minimize process development time by:
  - ⇒ Maximizing processing flexibility.
  - ⇒ Minimizing pre-demonstration testing.
  - ⇒ Minimizing permitting requirements.
  - ⇒ Identifying areas of uncertainty.
  - ⇒ Designing to overcome uncertainty.
- Minimize potential cost to convert demonstration unit to small-scale production unit.
- Identify potential enhancements for demonstration unit.
- Identify potential enhancements for a production embodiment.
- Minimize plant cost.

Minimizing community and worker exposure was the first design objective. Essentially four goals were sought to aid in meeting this objective: First the soil was to be converted into a slurry as quickly as possible (to minimize dust production and increase ease of handling). Second, dust production was to be minimized prior to producing the slurry. Third, the treated soil was to be mechanically extracted from the reactor. Finally the soil processing and treating units were to be separated. A conscious decision was made not to engage in dust collection because of the increased level of technical complexity involved. Instead, it was felt that dust control would be minimized by

moistening all dry soils prior to entering the facility (during the excavation). However, if field controls cannot be implemented, the system will be modified to allow the soil to be moistened prior to entering the system. One possibility is to add spray nozzles at the entrance of the pug mill and surge bins. In addition, covers will be placed over the bins above the pug mill and surge hopper to minimize the potential for dust escaping these units. The elevator and screw conveyor shall be operated at slow speed to minimize excess agitation and potential dust production. The speed of these units will be adjusted using variable speed motors, the actual speed to be used has not been established.

Separation of the soils processing and treatment units was also considered advantageous for decreasing the exposure risk because separation:

- Enables treatment remote from the soil processing unit.
- Enables treatment remote from soil excavation.
- Increases the capacity to isolate the treatment facility from facilities near the excavation area.
- Minimizes the potential for re-contaminating treated soil.
- Minimizes equipment exposure to agent and thus lowers the amount of equipment requiring decontamination.

The second objective was to demonstrate feasible commercial embodiment. To meet this objective, in TVA's opinion, two technical goals have to be met. First, the ability of peroxysulfate to efficiently mineralize chemical warfare agents in soil should be demonstrated at the pilot plant level. Second, the ability to safely handle the movement of contaminated soil from the field to the soil treatment unit should be demonstrated.

The first issue is addressed in the overall design of the soil treatment unit. The second is addressed in the design of the soil processing unit.

The third objective is to minimize process development time. This issue is important to minimize development cost and expedite movement to commercial embodiment. Essentially there are four elements to this objective: maximize process flexibility, minimize pre-demonstration testing, minimize permitting requirements; and identify areas of uncertainty and design to overcome uncertainty. Maximizing process flexibility involves the following elements:

- Enable the processing of a wide range of soil types.
- Arrange a plant layout that allows for reconfiguration -- to cope with unexpected soil handling characteristics.
- Minimize manual handling of contaminated soils.

To handle a wide range of soil types, two types of equipment were incorporated into the design: a pug mill to condition solids for easier handling and a ball mill to crush oversized materials. Use of this equipment should facilitate the handling of a range of soils including sand and rocky clays.

To cope with unexpected handling problems, a means of bypassing the ball mill and manually loading the soil treatment unit was devised. In addition, a reactor was selected which can double-up as a ball mill in event that the ball mill in the soil processing unit must be bypassed.

Minimizing the manual handling of contaminated soil is accomplished in the overall design of the soil processing unit and by the selection of a reactor that allows the removal of treated soil by mechanical means.

Minimization of pre-demonstration testing is also important to the minimization of process development time. Prior to conducting demonstrations with contaminated soil, it will be necessary to pre-test the facility with uncontaminated soil. Pre-tests are necessary both to measure dust production levels of the specific soil and to adjust/calibrate process equipment to soil characteristics. Process equipment requiring adjustment/calibration includes the: pug mill (tooth spacing adjustment), surge bin (charting soil weight versus height in bin), screw conveyor (charting soil feed rate against conveyor speed), and ball mill (conducting grind tests to establish the ball charge). Grind tests are especially time consuming. Batch type ball mills take less time to calibrate than continuous feed mills; because, the ball charge needn't be varied to handle the particle size distribution of the soil. Therefore, the design team chose to use a batch type ball mill. Use of batch systems also offers greater flexibility; since, grinding times can be altered should the soil's characteristics change.

To minimize process development time it is also desirable to minimize permitting time. Initially the soil treatment unit was envisioned with a solids filtering system just downstream of the rotary reactor. However, this approach was abandoned in favor of a drying system in which water is evaporated from the reactor, recovered by condensation, and recycled to the ball mill. At the end of the job, when the process water is being purged from the system, the water may be:

- Discharged as a liquid.
- Discharged as steam.
- Or collected and disposed of as if it was a hazardous material.

Using an evaporative system greatly lowers the volume of process water to be disposed of, leaves disposal options open, and limits NPDES permitting issues (permitting for cooling water discharge will still be required).

However, there is a cost associated with the use of an evaporative system. The peroxydisulfate process produces water soluble salts, mainly potassium sulfate, which remain in the soil. Had a soil filtration system been used, the soluble salts would have been flushed from the soil. The production of these salts is minimized by the use of calcium hydroxide as the neutralizing agent – resulting in the production of water insoluble gypsum ($CaSO_4$). However, the anticipated soil salt concentrations are between 0.5 to 5.5 percent by weight (assuming the treatment of soil contaminated with 1000 ppm agent). The variations in anticipated salt content depend upon the type of chemical agent being removed and its concentration in soil.

The use of an evaporative system was considered an acceptable compromise for this design since the units' commercial goal was to treat small soil volumes and the primary salt produced, potassium sulfate, is a common fertilizer. However, the soil produced by the demonstration plant will have to be applied to the land as a fertilizer or disposed of, due to high salt content. In a commercial scale plant, salt removed can be achieved by using additional washing, filtration (or other soil separating devices), and evaporative equipment.

The design of salt removal equipment was considered beyond the scope of this project. Detailed information about the specific soils being processed would be needed before this equipment could be designed. Because a demonstration site has not been selected, this information is not available. Furthermore, avoiding the use of a salt removal system at this point in process development helps minimize process development time by reducing plant complexity.

To minimize process development time, it is also necessary to minimize uncertainty. Currently it is unclear whether the peroxysulfate process will be able to treat agent that has migrated deep within the cracks, crevices, and pore space of rocks. To mitigate this uncertainty, as well as other considerations, grinding capacity was added -- in the form

of the ball mill and as well as within the reactor itself. These actions should help overcome this issue at minimal cost.

Minimizing the potential cost of converting the demonstration unit to a small scale production unit was the fourth objective of this project. Essentially, this objective was reached by incorporating a high level of flexibility into the existing design.

Identifying potential enhancements for the demonstration and commercial embodiments were the fifth and sixth objectives of this project. These enhancements include items that are desirable, but not absolutely necessary for the operation of a demonstration unit -- where cost is often an issue. Several potential enhancements were identified as follows:

- Injection of peroxysulfate solutions at earlier stages of the process.
- Allowing for pressurization of the rotary reactor/dryer.
- Designing a salt removal system.
- Adding a heater to the water recycle line between the soil processing and treatment units to aid in process decontamination.
- Use of a refrigeration unit in the condenser.
- Adding weight cells to the pug mill, surge hopper, ball mill, and reactor.
- Adding a densometer to the slurry line between the ball mill and reactor.
- Automating treated soil sampling and handling (production embodiment only).
- Consolidation of excavation and soils processing unit into a single mobile unit (production embodiment only).

In some cases it may be advantageous to pre-treat the soil with a peroxysulfate solution either during excavation or upon entering the process. Both HD and VX degrade at room temperature upon exposure to peroxysulfate solution, so pretreatment may be advantageous when dealing with these components. The advantage of pretreatment is that degrading the chemical agents at an early stage may substantially increase the ability to safely operate the facility. The disadvantages are:

- The corrosiveness of this solution is likely to affect all of the equipment in the soils processing unit since this equipment is constructed of carbon steel. (In contrast, exposed equipment in the soils treatment unit is constructed of stainless steel.)

- Fugitive off-gas will be produced as hydrocarbons present in the soil react with the oxidant (peroxysulfate).

- Off-gas production may impact the operation of downstream equipment, particularly the slurry pump.

- Uncontrolled mixing of hydrocarbons and oxidant present a potential fire hazard. This might be an issue, for example, when mixing with soils containing a high level of humus.

Not implementing this option helped keep equipment costs down, minimized potential hazards, and assured viable operation of the current design.

Allowing for the pressurization of the rotary reactor/dryer was also considered. Carbon dioxide gas will be produced as the peroxysulfate reacts with hydrocarbons in the soil. In the current design, this gas is allowed to escape via a vent in the reactor that leads to the condensing system and ultimately to the atmosphere via the carbon filter. However, this open line may allow fugitive agent to drift from the reactor into the condensing system during the treatment process. One option for preventing fugitive drift would be to seal the reactor and allow the pressure in the vessel to build until the reactions are complete. Then the gases could be vented and the slurry dried. Discussions with vendors indicated that reactors capable of withstanding pressurization were available. However, for purposes of demonstration, this option was not implemented due to cost constraints and the need for supplemental evaluation prior to implementation. This option should be considered for implementation in a commercial unit. Aspects of this

option that would require evaluation prior to implementing the use of pressurized reactors include:

- The degree of pressurization required considering the level of contamination, type of soil, and amount of hydrocarbon present.

- The impact of pressurization on reaction equilibrium or reaction rates.

- Whether the filter within the existing reactor will be sufficient to minimize fugitive drift.

- Whether the added expense for a pressurized reactor would be cost effective.

Adding a heater to the water recycle line between the soil processing and treatment units could enhance process decontamination. Unlike HD or VX, GB merely degrades to a less toxic substance when degraded with peroxysulfate at ambient temperature. By adding a heater to the recycle line, it would be possible to heat the solution being recycled between the recovery tank and ball mill thus assuring a higher level of decontamination. This option was not implemented in this design because alternate means of heating may be possible and keeping cost low was a primary objective.

Use of refrigeration in the condenser was considered as a means of eliminating the need for cooling water discharge and lowering water vapor emissions. However, for the purpose of a demonstration the use of refrigeration was avoided in the interest of cost control. Use of refrigeration should be evaluated for use in a commercial scale unit.

Use of weight cells to monitor the weight of materials in the pug mill, surge hopper, ball mill, and reactor was considered. Although the use of these devices may be valuable for monitoring the flow of materials, use of these devices was not implemented in the

interest of cost control. The plant is currently instrumented for visual monitoring and estimation of weight parameters.

The use of a densometer on the line between the ball mill and reactor was considered. This device would be used to measure the solids content of the slurry flowing between the ball mill and reactor. This device would be useful to assure that the line between the ball mill and reactor does not plug. The current design calls for visual inspection of fluid flow to the slurry pump. When the slurry flow from the ball mill begins to diminish, a slug of pure water is directed into the slurry pump to flush the line of solids prior to shutting down the slurry pump. The advantage of using a densometer is that the slurry line can be completely sealed. Otherwise, either a glass insert must be installed into the slurry line, to allow visual inspection, or an inspection port must be left open on the slurry pump (a bowl type sand pump) so that the diminished flow can be seen. Currently use of a glass insert is envisioned. Because manual methods have been used successfully in other TVA processes, use of a densometer was omitted to control cost. Use of a densometer should be considered in any evaluation of a commercial unit.

Once the demonstration plant has been shown to be effective, then improvements could be made to enhance the operation of a production unit. Potential enhancements include:

- Addition of a salt removal system.

- Integration of the soil excavation equipment and processing unit into a single, remotely controlled, mobile unit. Here a mobile processing unit capable of excavating, separating, grinding, slurrying, and pumping the soil to the treatment unit is envisioned. Similar equipment is used in the mining industry.

- Addition of dust control equipment for use around the soil processing units (pug mill, elevator, surge bin, and screw conveyor).

- Addition of dust control, automated sampling, and soils handling equipment for use at the discharge of the rotary reactor/dryer in the soils treatment plant.

3.5.5 Process Limitations and Advantages

Interest in remediating chemical agent contaminated soils is relatively new to the Department of Defense. In the past it was commonly believed that chemical warfare agents degraded in the soil with time and exposure to the elements; hence, emphasis was not placed on soils decontamination. This view has changed and interest in soils decontamination has increased. However, because this is a new field, most of the technology being examined is at the conceptual stage. The conceptual design presented here is among the first process designs to specifically address soil decontamination, therefore, it is somewhat difficult to compare alternatives at this time. The primary ex-situ alternative appears to be hydrolysis followed by bio-remediation. No conceptual designs of such a unit were found, however the general concept is to treat soil with hot water at 90 °C; this results in the degradation of chemical warfare agents, by hydrolysis, to less toxic materials. The water is then evaporated and the contaminated soil treated by biological means, presumably by composting, to remove the degradation by-products. One of the primary disadvantages of this process is that some of the by-products produced are toxic, therefore, post-treatment of the soil is necessary.

In comparison, the peroxysulfate process has demonstrated complete mineralization of most chemical warfare agent simulates (99.999 to 99.99999% mineralization depending upon component). In addition, the degree of degradation is thought to be higher than indicated above, because these figures are based on research data that was limited by equipment detection limits. Due to this advantageous chemistry, the peroxysulfate process is: low in residuals production, produces no toxic agent related by-products, and does not require post-treatment of the soil. In addition, the technology enjoys the advantages of :

- Simple process design
- Easy operability
- High transportability

The primary disadvantages of the process is that the peroxysulfate oxidants may react with organic components in the soil and, depending upon the level of agent contamination, salt concentrations in the soil may by high. The high salt concentration issue is mitigated by the fact that the salts are primarily potassium sulfate, a common fertilizer which can be applied to land.

3.5.6 Construction Cost Estimate

The estimated total cost (conceptual grade) to design and construct a transportable demonstration plant, including both the soils processing unit and the soil treatment unit, is $443,981. Should construction of only the soil treatment unit be desirable, then the cost would be $308,173. These estimates assume that the demonstration plant would be constructed as described above at TVA's facility at Muscle Shoals, AL. The estimates include the following components:

- Engineering design as related to the construction of the units described.
- Equipment and materials selection and purchase.
- Design and construction of the process units.
- Basic instrumentation (excluding MINICAMS).
- Material balance.
- Design drawings.
- Operating manual.

These estimates do not include:

- Contingency (15 percent recommended).
- Construction of containment buildings or similar structures.
- Reevaluation, optimization, or improvement of design components.
- Studies unrelated to direct construction (e.g., evaluations of process stability, reliability, or robustness; management of process residuals; scale-up requirements; etc.).
- Studies related to process risk/hazard assessment.
- Test plans.
- Health and safety plans.
- Chemical detection equipment (MINICAMS).
- Plant decontamination equipment.
- Laboratory testing equipment.
- Utility connections.
- Operating equipment (fork lifts, drums, Roura hoppers, etc.).
- Plant shake down or testing (except for mechanical rotation).
- Preparation for transportation from the construction site.
- Transportation of plant to another site.
- Installation at another site.
- Demonstration plant operations.

Identifying and costing the items above was beyond the scope of the current study.

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SECTION 4

CONCLUSIONS

4.1 Background

Peroxymonosulfate (HSO_5^-) and peroxydisulfate ($S_2O_8^{2-}$) are strong oxidants capable of degrading chemical warfare agents. Previous research with aqueous solutions (not containing soil) have shown that, at room temperature, the rates of reaction for VX and HD oxidation are rapid, but GB is not readily oxidized unless the peroxysulfate compounds are activated by heat or metal ion catalysis to form sulfate radical anions (SO_4^-). This research also indicated that, at moderately elevated temperatures (60-90 °C), peroxydisulfate rapidly mineralizes VX, HD, and GB. This study expands this base of knowledge by demonstrating that peroxysulfates are capable of remediating chemical warfare agent simulant contaminated soils.

4.2 Study Results

4.2.1 Reaction Specificity

Application of peroxysulfate oxidation to chemical warfare agent soil remediation requires that the oxidants have substantial selectivity for the target compounds. Otherwise, the oxidizing agents will be consumed by soil and other non-target materials. Bench-scale investigations were undertaken using Raman spectroscopy to quantify and speciate oxidant levels, and using various chromatographic techniques to quantify chemical warfare agent simulants and degradation products.

Kinetic data and product distributions from these studies demonstrated that peroxysulfate compounds have significant selectivity for chemical warfare agent simulants. The rates of degradation of peroxymonosulfate in soil slurries were substantially lower than the rates of decomposition in the presence of simulants indicating that peroxymonosulfate reacts with the simulants significantly more rapidly than it reacts with components in the soil. Consistent rates were observed for peroxydisulfate decomposition in soil slurries in the presence and absence of agent simulants. This result does not imply that peroxydisulfate is non-selective for simulant oxidation, but is the result of the reaction being controlled by the formation of the sulfate radical – the rate determining step for most peroxydisulfate reactions. The rate of sulfate radical anion decomposition could not be measured directly, but based on the rapid degradation of the agent simulants in soil slurries, the sulfate radical anions must exhibit substantial selectivity for oxidation of the target compounds.

4.2.2 Reaction Products

At ambient temperature (22 °C) peroxymonosulfate reacts almost instantaneously with the HD simulants (chloroethyl ethylsulfide and chloroethyl phenylsulfide), however, the reaction produces sulfone oxidation byproducts which do not further degrade.

At elevated temperature, peroxydisulfate detoxifies HD more rapidly than peroxymonosulfate. Furthermore, the peroxydisulfate degrades both the HD simulants and their sulfone oxidation products. The ultimate products of the reaction were not determined, but based on previous results, it can be assumed that the HD simulants are completely mineralized (oxidized to CO_2, Cl^-, and SO_4^{2-}) in the peroxydisulfate reaction. This ability to rid the contaminated soils of organic byproducts makes peroxydisulfate a promising compound for soil remediation. Since soils are decontaminated instead of personnel or equipment, the added time (~3 hours) and relatively (75 °C) high temperatures required for peroxydisulfate treatment are acceptable.

Peroxymonosulfate is not a suitable reagent for treating GB contaminated soils. Peroxydisulfate, however, was capable of reducing the GB simulant, diisopropyl methylphosphonate, in soils to concentrations below detection limits (< 0.048 mg/L) within an hour. The simulant was readily mineralized in aqueous solution, but substantial concentrations of methylphosphonic acid remained when the reaction was carried out in soil slurries. Apparently there was sufficient competition for oxidative equivalents by soil components to prevent the complete mineralization of reaction products.

Both peroxymonosulfate and peroxydisulfate rapidly reduced the concentrations of the VX simulant, O-ethyl S-ethyl phenylphosphonothioate, to concentrations below detection limits (< 0.0063 mg/L) in both aqueous solution and soil. Phosphonate reaction products remained after the oxidation by peroxymonosulfate, but evidence for mineralization of the simulant was found in the reaction with peroxydisulfate. In each peroxydisulfate reaction (both in solution and in soil slurries), the VX simulant degraded at a constant rate and evidence for mineralization was obtained. The competition for oxidative equivalents by the soil does not appear to be as severe as in the case of the GB simulant. However, it did take approximately ten hours to degrade the reaction intermediates (O-ethyl phenylphosphonate).

The development of a conceptual design for the small (750 pounds of soil per shift) batch demonstration plant indicate that unit could be constructed for approximately $450,000. The plant is designed to be transportable and could be used both as a demonstration plant and as a post demonstration treatment facility.

4.3 Recommendations for Future Work

Due to the promising results listed above, TVA RM recommends that work on the peroxysulfate process be continued as a potential demonstration program. This program is envisioned to be executed in five phases as follows:

- Phase I - A laboratory study in which chemical warfare agents (HD, GB, and VX) would be used to verifying the results of the current study, confirm agent mineralization, and to develop a better understanding of the underling chemistry.
- Phase II - A laboratory study focused on the collection of process design and Health and Safety related information.
- Phase III - Design of a demonstration facility.
- Phase IV - Construction of a demonstration facility.
- Phase V - Demonstration of the technology.

Use of the five phase approach will allow periodic review of project progress between phases and provides opportunities to periodically reassess project viability as the program progresses.

The primary goal of the Phase I laboratory study is to facilitate an understanding of the chemistry and thereby increase public perception of acceptable viability by the AEC, TVA RM, government regulators, the academic community, and the community at large. This will be accomplished by:

- Establishing degradation rates using chemical warfare agents.

- Identifying by-products produced with chemical warfare agents.
- Conclusively determining the levels of mineralization of agent simulants using radio-labeled chemicals (^{14}C and ^{35}S for CEPSI; ^{14}C and ^{32}P for DIMP; and ^{14}C, ^{32}P, and ^{35}S for OSDEPPT).
- Identifying the reasons peroxysulfates tend to be selective for chemical warfare agents over other compounds by conducting:

  ⇒ A sorption/desorption and kinetic study using agent simulants to asses whether reaction rates are desorption rate limited.

  ⇒ A study comparing the oxidation rates of chemical warfare agents or simulants compared to that for soluble humic material and metals.

- Identifying the neutralizing agent (base) to be used by:

  ⇒ Identifying of the amount of base required.

  ⇒ Identifying and quantifying of commercial (fertilizer) salt content.

  ⇒ Identifying and quantifying of non-commercial salt content.

  ⇒ Assessing the impact of salt content on potential land application.

  ⇒ Determining the working characteristics of the solids produced.

- Conduct environmentally related tests on treated and neutralized soil originally contaminated with chemical warfare agents including:

  ⇒ EPA toxicity, leaching, and reactivity tests.

  ⇒ Identification of other toxic by-products (chemical warfare by-products, fluoride salts, metals, etc.)

At the end of Phase I, program participants should have sufficient information about the chemistry involved, the characteristics of the treated soil, and the processes ability to detoxify agent contaminated soil to confidently recommend activation of Phase II.

The primary goal of Phase II is to collect information vital to the design or operation of the demonstration unit. This will be accomplished by:

- Collection of vital process design information including:

  ⇒ Developing boiling point curves for the evaporative system.

  ⇒ Identifying the volume of by-product gas produced during soil treatment.

  ⇒ Identifying by-product gas composition during soil treatment.

  ⇒ Identifying the temperature rise upon the addition of neutralizing agent.

  ⇒ Identifying non-condensable gas volume during evaporation.

  ⇒ Identifying non-condensable gas composition during evaporation.

- Collection of non-vital process improvement information including:

  ⇒ Investigating the possibility of reducing in oxidant usage (current usage is optimized to assure as complete a level of mineralization as possible).

  ⇒ Investigating the possibility of accelerating chemical warfare agent and by-product degradation by the continuous addition of oxidant. (The initial addition of excess oxidant can lead to a scavenging of sulfate radicals and hence is not recommended).

  ⇒ Investigate the use of quenching agents to accelerate the breakdown of excess oxidants. (Currently, sufficient drying time is allowed to assure oxidant breakdown prior to discharge).

- Collection of health and safety information required to assure safe operation of the demonstration unit as well a timely communication with regulators in the highly unlikely event of a unintentional discharge during demonstration. This information includes.

  ⇒ Determining the expected concentration of toxic materials in slurried process water prior to treatment.

  ⇒ Determining the expected concentration of toxic materials in reactor vapors during treatment.

  ⇒ Determining the expected concentration of toxic materials, if any, in aqueous phase after treatment but prior to evaporation.

  ⇒ Determining the expected concentration of toxic materials, if any, in soil after treatment prior to evaporation.

  ⇒ Determining the expected concentration of toxic materials, if any, in vapor during evaporation.

  ⇒ Determining the expected concentration of toxic materials, if any, in the condensate during evaporation.

At the end Phase II, program participants should have sufficient information about the process to assure ease of design and an understanding of potential process hazards.

The identification of specific goals for the design, construction, and demonstration phases (Phases III, IV, and V) of this proposed project are not outlined here, since TVA RM feels it would be prudent to examine the results of Phases I and II before suggesting any specific goals for these phases.

4.4 Summary

This project was initiated to determine the feasibility of using peroxysulfate based oxidants to remediate soils contaminated with GB, HD, and VX. The project was

designed to determine whether soil-borne agent simulants will degrade when exposed to slurries containing the oxidants.

The study results indicate that, at temperatures ranging between 75 and 90 °C, peroxysulfates degraded between 99.999 to 99.99999 percent of the exposed simulants within three hours. Evidence of nearly complete mineralization of the HD and VX simulants was observed when peroxydisulfate was used. However, the GB simulant's reaction intermediates were not completely mineralized and the VX simulant's reaction intermediates took about ten hours to degrade.

Due to these promising results, TVA RM is recommending that work on the peroxysulfate process be continued.

SECTION 5

ACKNOWLEDGMENTS

Acknowledgments are made to James L. Horton and Amanda A. Gordon for performing GC/MS analyses, aiding in the identification of reaction intermediates.

Thanks are also expressed to Richard A. Almond and Joseph J. Hoagland for contributing ideas and direction to the study.

APPENDIX A

METHODS AND PROCEDURES

Appendix A-1- Method ASTM-D422: Soil Particle Size by Sieve Analysis and Hydrometer

Tennessee Valley Authority

Analytical Laboratory of Environmental Applications
Environmental Research Center
Muscle Shoals, AL 35662

Procedure Number : AP-0061

Title: Soil Particle Size Analysis by Sieve and Hydrometer - ASTM D421 and ASTM D422

Signature	Title	Date
Prepared by: William J. Rogers	QA Officer	4/30/97
Concurred: Eugene A. Zarate	Laboratory Section Leader	4/30/97
Concurred:		
Concurred:		
Approved: Joseph J. Hoagland	Manager	4/30/97

Revision	R0					
Control Date	30-Apr-97					

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1.0 PURPOSE

To determine particle size distribution of soil for gravel, sand, silt, and clay fractions by sieve and hydrometer methods.

2.0 SCOPE

This procedure applies to soil and soil-like substances which are insoluble in water and have a density approaching that of soil.

3.0 SUMMARY

3.1 ASTM-D421 - A dry soil sample is sieved through a #10 sieve. The retained fraction is ground gently, then sieved again. The retained fraction is washed, dried and weighed. This is the gravel fraction.

3.2 ASTM-D422 - A portion of the sample which passed the #10 sieve is allowed to stand overnight in a 4% sodium metaphosphate solution and then dispersed in a blender. It is placed in a 1-liter sedimentation cylinder and the liquid is brought to volume. The soil is suspended, and the density of the soil suspension is measured with a hydrometer at 0.5, 1, 2, 5, 10, 15, 30, 60, 250, and 1440 minutes. The weight of soil in suspension is derived from the hydrometer readings. Utilizing Stoke's law, particle size is determined from sedimentation rate. In this fashion, the percentage of the soil sample as a function of particle size may be determined.

After hydrometer analysis, the sample is then washed through a #200 sieve. The fraction retained on the #200 sieve is the sand fraction by wet sieve method.

4.0 REFERENCES

4.1 ASTM-D421-85, "Standard Practice for Dry Preparation of Soil Samples for Particle-Size Analysis and Determination of Soil Constants", American Society for Testing and Materials.

4.2 ASTM-D422-63 (Reapproved 1990), "Standard Test Method for Particle-Size Analysis of Soils", American Society for Testing and Materials.

5.0 RESPONSIBILITIES

5.1 It is the responsibility of the laboratory manager to ensure that this procedure is followed.

5.2 It is the responsibility of the team leader to review the results of the procedure.

5.3 It is the responsibility of the laboratory analyst to follow this procedure and to report any abnormal results or unusual occurrences to the laboratory team leader.

6.0 REQUIREMENTS

6.1 Prerequisites

None.

6.2 Limitations and Actions

6.2.1 The first two hydrometer readings at 0.5 and 1.0 minutes are the most critical and should be made as close to the second as possible.

6.2.2 If subsequent hydrometer readings cannot be made at the scheduled time, note the exact time so that corrections may be made in the calculations.

6.3. Apparatus/Equipment

6.3.1 Sieve - brass or stainless steel, #10 (2.00 mm) size.

6.3.2 Sieve - brass or stainless steel, #200 size.

6.3.3 Blender - household or laboratory grade.

6.3.4 Sedimentation Cylinder - One liter, glass.

6.3.5 Hydrometer, soil test - Type 152H.

6.3.6 Thermometer - laboratory grade for measuring ambient temperature.

6.4 Reagents and Standards

6.4.1 4% Sodium Metaphosphate solution - dissolve 40 grams of sodium metaphosphate (also known as sodium hexametaphosphate) in 900 ml deionized water and bring to a volume of one liter. Larger quantities may be mixed in the same proportion.

6.4.2 N-Amyl Alcohol - used as a defoaming agent.

6.5 Quality Control Sample Requirements

6.5.1 No standard reference soil is available to test this procedure. Duplicate samples may be run at the request of the customer.

7.0 PROCEDURE

7.1 Determination of Gravel Fraction - ASTM-D421

7.1.1 Allow the sample to air dry. Select approximately 115 g of sandy soil or approximately 65 g of silt or clay soil. Weigh the sample and record the weight as the air-dried weight. This weight is uncorrected for hygroscopic moisture.

7.1.2 Separate the test sample by sieving through a #10 sieve. If no gravel is present, proceed to Step 7.2.

7.1.3 Grind the fraction retained on the sieve in a mortar with a rubber-covered pestle or gloved thumb until the aggregations of soil particles are broken up into separate grains.

7.1.4 Separate the ground soil into two fractions by sieving with a #10 sieve. Combine the two fractions which have passed the sieve.

7.1.5 Wash the retained fraction free of all fine material by passing the sieve under running water. Do not retain fines.

7.1.6 Dry it at 105°C and weigh it. Record the mass as the mass of coarse material.

7.2 Sand, Silt and Clay Fractions by ASTM-D422

7.2.1 Weigh approximately 50 g of clay and silt soil or 100 g of sandy soil from the portion which passed the #10 sieve.

7.2.2 Weigh an auxiliary portion of 10 to 15 g for moisture determination. Determine moisture by drying the sample to constant weight at 105°C. Record the weight of the container, weight of the sample and container before drying, and the weight of sample and container after drying.

7.2.3 Place the sample in a beaker and cover it with 125 ml of 4% sodium metaphosphate solution. Allow it to soak for at least 16 hours.

7.2.4 Disperse the sample in a blender for one minute. For highly plastic soils, disperse for longer periods of time (up to 15 minutes) until no lumps or aggregations are noted.

7.2.5 Immediately after dispersion, transfer the slurry from the blender into a one-liter glass cylinder with deionized water. Bring the cylinder to volume.

7.2.6 Prepare a separate cylinder with 125 ml of 4% sodium metaphosphate solution diluted to one liter as a reference cylinder.

7.2.7 Stopper the cylinder with a rubber stopper. Turn the cylinder upside down and back for a period of 1 minute, noting the ending time. Any soil adhering to the bottom of the cylinder, should be suspended by shaking during the first few turns. Do not agitate more than necessary, to minimize foam which interferes with hydrometer readings.

7.2.8 Set the cylinder on a stable surface and place the hydrometer into the suspension. Take readings at 0.5, 1, 2, and 5 minutes. Add n-amyl alcohol dropwise as a defoaming agent, as needed. The first two readings are the most critical. Read the hydrometer at the top of the meniscus.

7.2.9 Place a thermometer in one cylinder at a convenient time during the first 10 minutes and note the temperature.

7.2.10 Place the hydrometer into the reference cylinder and take a reference reading.

7.2.11 Continue taking hydrometer readings from the soil suspension at 10, 15, 30, 60, 250, and 1440 minutes. With each reading past 15 minutes, take a reference reading from the reference cylinder as well. Record the temperature with each reading.

7.2.12 Repeat the process with each sample, scheduling blending, shaking, and readings so that all readings may be taken. If any reading cannot be made exactly at the scheduled time, note the actual time.

7.3 Sand

7.3.1 After completing the hydrometer analysis, transfer the suspension to a #200 sieve and wash with tap water until the wash water is clear. The portion retained on the sieve is the sand fraction (wet sieve method).

7.3.2 Transfer the material on the sieve to a suitable container and dry it in an oven at 105°C. Record the weight of the dried material.

7.4 Calculations and Recording Data

Data may be calculated on spreadsheets SIEVE and HYDROMET. Examples are attached in 10.1 and 10.2

Calculations in the spreadsheets utilize the equations below.

7.4.1 Percent Retained on #10 Sieve

$M10P = M10_O - M10R$

$P10 = 100 * M10P/M10_O$

%Gravel = 100 - P10

Where

P10 is the percent passing the #10 sieve
M10P is the mass passing #10 sieve
$M10_O$ is the mass originally split on the #10 sieve
M10R is the mass retained on the #10 sieve

7.4.2 Hygroscopic Moisture Correction Factor

$HMCF = M_{OD}/M_{AD}$

Where
HMCF is the hygroscopic moisture correction factor
M_{OD} is the mass of oven-dried soil
M_{AD} is the mass of air-dried soil

7.4.3 Percentage of Soil in Suspension

$MODH = MADH * HMCF$
$W = MODH * 100 / P10$
$R = R_{sus} - R_{ref}$
$P = (R * a / W) * 100$

Where
P is the percentage of soil in suspension at any given measurement time
R is the corrected hydrometer reading
R_{sus} is the reading in the soil suspension
R_{ref} is the reading in the reference cylinder

MODH is the mass of oven-dry soil used in the hydrometer test
MADH is the mass of air-dry soil used in the hydrometer test
W is the mass of the total sample represented by the mass of soil used in the hydrometer test.

a (or α) is the correction factor for differing specific gravity of soil particles. Use 1.00 unless a specific gravity other than 2.65 is known to apply. In that case, see ASTM D422, Table 1.

7.4.4 Diameter of Soil Particles

$$D = SQRT[(30 * n / (980 (2.65 - 1.00)) * L / T)]$$

Where

D is the diameter of soil particles in mm
n is the coefficient of viscosity of water in poises (varies with temperature) See Table 9.1
2.65 is the specific gravity of soil
1.00 is the specific gravity of water
L is the effective depth, the distance from the surface of the suspension to the level at which the density of the suspension is being measured (cm). L is calculated according to the following formula.

$$L = L1 + 0.5 * (L2 - (Vb / A))$$

L1 is the distance along the stem of the hydrometer from the top of the blub to the reading mark. (L1 is interpolated linearly from 10.5 cm for a reading of 0 g/L and 2.3 cm for a reading of 50 g/L)
L2 is the length of the bulb, 14.0 cm
Vb is the volume of the bulb, 67.0 cm^3
A is the cross-sectional area of the sedimentation cylinder, 27.8 cm^2
T is the time of the reading in minutes

7.4.5 Determination of Silt and Clay Fractions

ASTM utilizes particle diameters of 0.005mm and 0.074mm as the break points for clay and silt particles. (U. S. Department of Agriculture utilizes 0.002 and 0.050 mm.) See Note 9.2

To determine the silt and clay fractions, first plot the percentage of soil remaining in suspension, P, as a function of particle diameter, D, as calculated above. Interpolate between the points to find the percentages at the ASTM (or USDA) silt and clay break points using a logarithmic interpolation.

Example: for a 0.005 mm clay fraction

$P_{.005} = PR1 + (PR2 - PR1)* Log(0.005 / DR2)/[Log(DR1 / DR2)]$

Where

PR1 is the percent calculated for reading R1
PR2 is the percent calculated for reading R2
DR1 is the diameter calculated for reading R1
DR2 is the diameter calculated for reading R2

and DR1 and DR2 bracket 0.005 mm.

Example: 55.69% of a sample is less than 0.0058 mm and 49.72 is less than 0.0029 mm.

$P_{.005} = 49.72 + (55.69 - 49.72) * Log (0.005/0.0029)/[Log(0.0059/0.0029)]$

$= 49.72 + (5.97) * 0.23657/0.301029 = 54.4$

7.4.6 Percentage Passing #200 Sieve

$M_{Corr} = (100 - P10) * W / 100$

$M_{200P} = W - M_{Corr} - M_{200R}$

$P200 = M_{200P}* 100 / W$

M_{Corr} is the mass that would have been retained on the #10 sieve
M_{200P} is the mass passing the #200 sieve
M_{200R} is the mass retained on the #200

P10 and W are defined above.

7.4.7 Reporting

Report the values as

Percentage Passing 0.074 mm
Percentage Passing 0.005 mm
Percentage Passing #10 sieve(2.00 mm)
Percentage Passing #200 sieve (0.075 mm)

Also provide percentages at the USDA values of 0.002 and 0.050 mm if the customer requests them.

8.0 SAFETY

8.1 No particularly hazardous chemicals or operations are involved in this procedure. Observe routine laboratory safety precautions including wearing safety glasses and lab coat. Wear gloves when handling sodium metaphosphate. Avoid inhalation of dust.

9.0 NOTES

9.1 Viscosity of Water

Temperature °C	Viscosity in poise
15	0.01139
16	0.01109
17	0.01081
18	0.01053
19	0.01027
20	0.01002
21	0.009779
22	0.009548
23	0.009325
24	0.009111
25	0.008904
26	0.008705
27	0.008513
28	0.008327

9.2 Definitions of soil particle sizes have been promulgated by a variety of national and international bodies. Two are of primary interest in the US, those of the ASTM and of the USDA.

ASTM definitions are summarized as follows: clay (<.005mm), silt (<0.074 mm), fine sand, medium sand, and coarse sand (>2.00 mm), fine gravel, coarse gravel, and cobbles.

USAD definitions are summarized as follows: clay <0.002 mm), silt (<0.050 mm), very fine sand, fine sand, medium sand, coarse sand, very coarse sand, fine gravel (>2.00 mm), coarse gravel, and cobbles.

10.0 ATTACHMENTS AND APPENDICES

10.1 Spreadsheet SIEVE

Sieve analysis - ASTM D421 and D422
Gravel, Sand, and Clay/Silt Fractions

Analysis by _____
Date _____

Sample ID: 97-06-023	01A						
Dry Sieve for % Gravel (#10)	ASTM D421 Section 6.						
Sample Weight Sieved	127.00						
Total Weight - Container and Dry Residue	44.00						
Tare Weight - Container	13.00						
Weight Retained	31.00	0.00	0.00	0.00	0.00	0.00	0.00
Wet Sieve for % Sand (#200)	ASTM D422 Section 11.						
Sample Weight Sieved	50.42						
Total Weight - Container and Dry Residue	341.52						
Tare Weight - Container	331.68						
Weight Retained	9.84						
Percent Solids and Moisture @ 105 C	(Oven Dry Moisture)						
Container and Air Dry Sample	10.0400						
Container and Dry Sample	9.8500						
Tare Weight - Container	0.0000						
Weight sample	10.04	0	0	0	0	0	0
Weight Dry Sample	9.85	0	0	0	0	0	0
% Passing #10 Sieve (2.00 mm)	75.6%						
% Passing #200 Sieve (0.075 mm)	60.6%						
% Moisture	1.9%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%
Hygroscopic Correction Factor	0.9810757						
Oven-dry mass used in hydrometer test	49.465837	0	0	0	0	0	0
Mass of total Sample	65.43918						
Mass that would have been retained #10	15.973343	0	0	0	0	0	0
Total mass passing #200	39.625837	0	0	0	0	0	0

10.2 Spreadsheet HYDROMET

Particle Size Analysis of Soils - ASTM D422 - Hydrometer Method

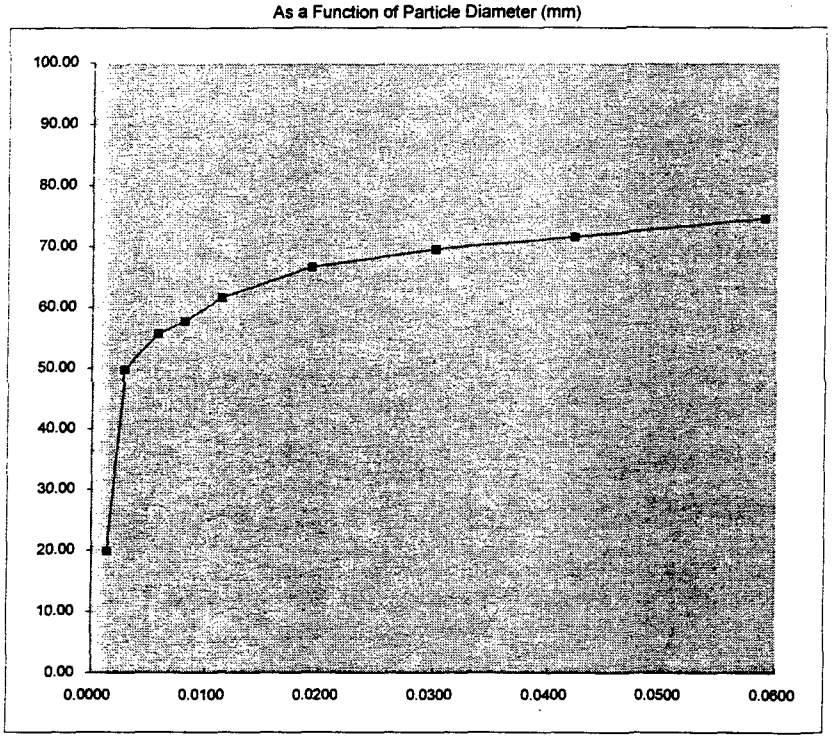
Sample ID: 95-12-021-01A

Time Minutes	Reading Type 152H	Correction for Blank	Corrected Reading	Weight (g)	% Passing #10 Sieve	Dry Weight Calculated	Percent Suspended	Hydrometer Depth	Particle Diameter	Interpolation at 0.005	at 0.074	at .002	at .050
0.5	42.5	5.0	37.5				74.59	9.3	0.0589		76.6		73.1
1	41.0	5.0	36.0				71.60	9.6	0.0422				
2	40.0	5.0	35.0	50.277	100	50.28	69.61	9.7	0.0301				
5	38.5	5.0	33.5	Temp			66.63	10.0	0.0193				
15	36.0	5.0	31.0	20.5		G-G1	61.66	10.4	0.0114				
30	34.0	5.0	29.0	% moisture		1.65	57.68	10.7	0.0082				
60	33.0	5.0	28.0				55.69	10.9	0.0058	54.4			
250	30.0	5.0	25.0	0		n (viscosity)	49.72	11.4	0.0029			35.4	
1440	15.0	5.0	10.0			0.01002	19.89	13.8	0.0013				
						From table		K ====>	0.0136345				

Percentage Passing	
0.074 mm	76.6
0.050 mm	73.1
0.005 mm	54.4
0.002 mm	35.4

ASTM utilizes 0.005 and 0.074 mm
USDA utilizes 0.002 and 0.050 mm

Percentage of Soil Remaining in Suspension
As a Function of Particle Diameter (mm)



Analysis by _____

Reviewed by _____

End of Procedure

Appendix A-2- Method AP-0048: Measurement of Diisopropyl Methylphosphonate (DIMP) by Gas Chromatography

Tennessee Valley Authority

Analytical Laboratory of Environmental Applications
Environmental Research Center
Muscle Shoals, AL 35662

Procedure Number : AP-0048

Title: Measurement of Diisopropyl Methylphosphonate (DIMP) by Gas Chromatography

Signature	Title	Date
Prepared by: John Grinstead	Research Chemist	3/3/97
Prepared by: William J. Rogers	Quality Assurance Officer	3/3/97
Concurred: James R. Pugh	Team Leader	3/3/97
Concurred:		
Approved: Joseph J. Hoagland	Manager	3/3/97

Revision	R0	R1				
Control Date	31-Jan-97	03-Mar-97				

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1.0 PURPOSE

This procedure describes actions required to measure diisopropyl methylphosphonate (DIMP) by gas chromatography for kinetic studies with various oxidants.

2.0 SCOPE

This method is applicable to determinations in water and soil slurries to determine relative concentration in kinetic studies.

3.0 SUMMARY

In a kinetic study, a series of samples is taken as a function of time under various reaction conditions. For each sample, the reaction is first quenched by chilling. The sample is extracted with ethyl acetate. The extract is injected and analyzed using a gas chromatography system equipped with a nitrogen/phosphorus detector (Thermionic Specific Detector or TSD).

4.0 REFERENCES

4.1 "The Determination of Diisopropyl Methylphosphonate and Dimethylmethyl Phosphonate in Water by Gas Chromatography, (Method No. AT8)," Version 2, Data Chem Laboratories, November 15, 1988.

4.2 "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods", SW-846, 3rd Edition, Most Recent Update (July 1992 with proposed methods dated November 1992)

Chapter 1, "Quality Assurance"

Chapter 4, "Organic Analysis"

Method 8000A, "Gas Chromatography"

4.3 "Thermionic Specific Detector", Varian Instrument Group/Walnut Creek Division, Publication Number 09-914089-00.

5.0 RESPONSIBILITIES

5.1 It is the responsibility of the laboratory manager to ensure that this procedure is followed.

5.2 It is the responsibility of the team leader to review the results of the procedure.

5.3 It is the responsibility of the laboratory analyst to follow this procedure and to report any abnormal results or unusual occurrences to the laboratory group leader.

6.0 REQUIREMENTS

6.1 Prerequisites

6.1.1 Sampling times are determined prior to starting this procedure from an experimental design or plan. Sampling times and pertinent experimental data are recorded in a research notebook.

6.1.2 Helium and hydrogen flows are adjusted to achieve the correct pattern ratio in a TSD test mixture as described in the detector operations manual.

6.1.3 Samples are chilled prior to delivery for analysis to quench the reaction.

6.2 Limitations and Actions

6.2.1 Quenching of the reaction by chilling should be done as soon as possible after sampling. Extraction should follow as rapidly as possible.

6.2.2 The TSD detector is capable of handling aqueous samples, however the removal of the analyte from the aqueous oxidant solution by extraction with ethyl acetate effectively stops the reaction and reduces problems with oxidants degrading column performance and chromatography in general.

6.2.4 The most effective use of resources in these kinetic studies requires timing of chromatography system startup and the chemical reaction being studied so that calibration samples are at the end of the run rather than at the beginning.

6.2.5 Deterioration of detector response to less than 75% of initial stable response may indicate the need to clean or replace the TSD ceramic bead.

6.3 Apparatus/Equipment

6.3.1 Analytical balance with 0.0001-gram sensitivity

6.3.2 120 ml amber bottles with Teflon-lined screw caps

6.3.3 Disposable glass pipettes

6.3.4 5 ml Plastic syringes and 0.45μm nylon filters

6.3.5 2 dram glass vials

6.3.6 Autosampler vials for Varian 8200 autosampler

6.3.7 A Varian 3400 gas chromatograph equipped with a Thermionic Specific Detector, a 1041 universal injector and a 15 meter DB5 530μ fused silica capillary column.

6.3.8 Vortex mixer

6.4 Reagents and Standards

6.4.1. Ethyl Acetate, EM Science Omni.Solv glass distilled suitable for LC, GC

6.4.2 Deionized water.

6.4.3 Diisopropyl methylphosphonate (DIMP) - reagent grade.

6.4.4 DIMP Standards - Various dilutions of reagent grade DIMP as outlined below. Store standards in the refrigerator when not being used.

6.4.4.1 Primary standard - dilute approximately 0.1g of DIMP (weighed to the nearest 0.1 mg) to 100ml with ethyl acetate.

6.4.4.2 Secondary standard - Dilute the primary standard 1 to 50 with ethyl acetate. (approximately 20 ppm).

6.4.4.3 Second primary standard - This standard is mixed from a separate lot of DIMP as a check against the original primary standard and to look for any tendencies for degradation of the standards. Dilute approximately 0.1 g of DIMP (weighed to the nearest 0.1 mg) to 100ml with ethyl acetate. Make dilutions of this solution as for the primary standard solution.

6.4.4.4 Calibration standards - dilute suitable volumes of the secondary standard with ethyl acetate to make individual standards from 0.5 to 20 ppm before each run.

6.4.5 Acetone, EM Science OmniSolv, suitable for high resolution GC coinjected with samples and used as a wash for the autosampler needle.

6.5 Quality Control Sample Requirements

6.5.1 Every tenth sample should be followed by a midpoint calibration standard run as a sample. Recovery should be 90 to 110% of the expected value.

6.5.2 With each batch of samples, run a laboratory control sample consisting of a sample with a concentration approximately equal to the midpoint of the calibration curve, but from the second primary standard stock. Recovery should be 90 to 110% of the expected value.

6.5.3 With each batch of samples, run a method blank through the extraction and analysis procedure.

6.5.4 Log and chart peak height of the initial midpoint calibration standard as an indicator of detector deterioration. See 6.2.5.

7.0 PROCEDURE

7.1 Calibration

7.1.1 Simultaneously with initiating the kinetic study under its planned experimental conditions, warm up the gas chromatograph.

7.1.1 Analyze a single 10 ppm standard at the start of the run. A complete set of standards is run following all experimental samples. The sample data are calculated from a linear regression fit of the standards utilizing chromatography workstation software.

7.1.2 A comparison is made of the peak height of the initial 10 ppm standard with that of previous runs to look for any major changes in response. See 6.2.5.

7.2 Procedure Instructions

7.2.1 Sampling and Extraction

7.2.1.1 According to the experimental design, pull each sample at the appropriate time and immediately chill it by immersing it in ice water.

7.2.1.2 Utilizing information from the experimental design as to the total amount of DIMP involved in the experiment, calculate the weight (or volume) of sample and volume of ethyl acetate needed to keep the concentrations within the calibration range. Record weights and volumes in the research notebook.

Note: Small amounts of water are soluble in ethyl acetate. At 50:1 the water will be dissolved completely in the ethyl acetate phase so that the actual dilution would be 51:1 in the final calculation. This is advantageous when extracting soil slurries because all water in the soil will be removed and extracted into the ethyl acetate phase.

7.2.1.3 Place the correct quantities of sample and ethyl acetate in a 2-dram vial. Cap the vial with a Teflon-lined cap.

7.2.1.4 Mix the sample and ethyl acetate on a vortex mixer for one minute.

7.2.1.5 Allow the extract to settle for approximately 5 minutes.

7.2.2 Place 1 ml of the ethyl acetate phase in an autosampler vial.

7.2.3 Load the samples into the autosampler and schedule the samples for analysis with the following operational parameters:

7.2.3.1 Gas Flow:

Carrier - Helium: 6 - 8 ml/minute
Makeup - Nitrogen 20 ml/minute
Auxiliary - Hydrogen 3.5 - 4.5 ml/minute
Air - 175 ml/minute

Pressure set at the regulator - Helium 80, Hydrogen 40, Air 60, Nitrogen 60

7.2.3.2 Temperature:

Injector: 225° C
Detector: 250° C
Oven: 70° C for 1.0 minute, then ramped at 20° C/minute to 225° C and held for 1.0 minute

Note: Run time including printout is 19 minutes.

7.2.3.3 Injection volume: 1 microliter (μL).

7.2.3.4 Set in solvent flush mode with acetone at 1 μL as follows:

Autosampler type	8200
Special Sample Mode	User Defined Sample
Solvent Select	(acetone)
Solvent Flush Sampling	Yes
Syringe Wash Time	20 seconds
Solvent Plug Size	1.0
Vial Needle Depth	90%
Uptake Speed	5.0 ul/second
Upper Air Gap	Yes
Lower Air Gap	Yes
Pause Time	1 second
Hot Needle Time	0.00 minutes
Injection Rate	5.0 ul/second
Needle Residence Time	0.00 minutes

7.2.3.5 Retention time is approximately 3.65 minutes.

7.3 Calculations and Recording Data

7.3.1 The calculations for the GC work are done by vendor-supplied software using the Varian Star Data Package.

7.3.2 Record all pertinent data such as sampling times, weights, volumes, peak areas, concentrations and reaction conditions in the research notebook.

7.3.3 Maintain copies of all workstation printouts.

7.3.4 Note any decisions to reject runs, decisions regarding peak identification, assessments of poor data, or the like on the workstation printouts or in the research notebook.

8.0 SAFETY

8.1 Handle all open samples containing DIMP and perform all transfers of this material in a hood.

8.2 Routine laboratory protective clothing (lab coat, gloves, and eye protection) is all that is required for this procedure .

9.0 NOTES

9.1 The tested concentration range in water is 0.5 to 20 mg/L

9.2 The MDL of DIMP has been determined to be 0.048 mg/L

9.3 Reporting Limit 0.5 mg/L to 20 mg/L, $r^2 = 0.9991$

9.4 Interferences - None noted.

9.5 Recovery - Extraction of DIMP from soil gave a recovery of 96.7 %.

9.6 Analysis rate - After instrument calibration, one analyst can analyze 25 samples in an 8 hour day (24-hour instrument day).

9.7 Chemical Abstract Service (CAS) numbers and selected physical properties of the analyte are:

Analyte	CAS#	m.p.	b.p.	Density	LD_{50}
DIMP	1445-75-6	20°C 1	90°C	0.976 g/ml	100 mg/kg

9.8 The reagent material used to make analytical standards for this method was:

a) DIMP, Alfa/Aesar Johnson Matthey stock #30301 lot #F02F07 98+%

b) DIMP, Alfa/Aesar Johnson Matthey stock #30301 lot #B21G16 98+%

10.0 ATTACHMENTS AND APPENDICES

None

End of Procedure

Appendix A-3 - Method AP-0049: Determination of O-ethyl-S-ethyl phenylphosphonothioate in Water and Soil Slurries by Gas Chromatography

Tennessee Valley Authority

Analytical Laboratory of Environmental Applications
Environmental Research Center
Muscle Shoals, AL 35662

Procedure Number : AP-0049

Title: Determination of O-Ethyl-S-Ethyl Phenylphosphothioate in Water and Soil Slurries by Gas Chromatography

Signature	Title	Date
Prepared by: John Grinstead	Research Chemist	3/3/97
Prepared by: William J. Rogers	Quality Assurance Officer	3/3/97
Concurred: James R. Pugh	Team Leader	3/3/97
Concurred:		
Approved: Joseph J. Hoagland	Manager	3/5/97

Revision	R0	R1				
Control Date	31-Jan-97	03-Mar-97				

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1.0 PURPOSE

This procedure describes actions required to measure O-ethyl-S-ethyl phenylphosphonothioate by gas chromatography for kinetic studies with various oxidants.

2.0 SCOPE

This method is applicable to determinations in water and soil slurries to determine relative concentration in kinetic studies.

3.0 SUMMARY

In a kinetic study, a series of samples are taken as a function of time under various reaction conditions. For each sample, the reaction is first quenched by chilling. Following this, the sample is extracted with ethyl acetate. The extract is injected and analyzed using a gas chromatography system equipped with a nitrogen/phosphorus detector (Thermionic Specific Detector or TSD).

4.0 REFERENCES

4.1 "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods", SW-846, 3rd Edition, Most Recent Update (July 1992 with proposed methods dated November 1992)

Chapter 1, "Quality Assurance"

Chapter 4, "Organic Analysis"

Method 8000A, "Gas Chromatography"

4.2 "Thermionic Specific Detector", Varian Instrument Group/Walnut Creek Division, Publication Number 09-914089-00.

5.0 RESPONSIBILITIES

5.1 It is the responsibility of the laboratory manager to ensure that this procedure is followed.

5.2 It is the responsibility of the team leader to review the results of the procedure.

5.3 It is the responsibility of the laboratory analyst to follow this procedure and to report any abnormal results or unusual occurrences to the laboratory group leader.

6.0 REQUIREMENTS

6.1 Prerequisites

6.1.1 Sampling times are determined prior to starting this procedure from an experimental design or plan. Sampling times and pertinent experimental data are recorded in a research notebook.

6.1.2 Helium and hydrogen flows are adjusted to achieve the correct pattern ratio in a TSD test mixture as described in the detector operations manual.

6.2 Limitations and Actions

6.2.1 Quenching of the reaction by chilling should be done as soon as possible after sampling. Extraction should follow as rapidly as possible.

6.2.2 Reactions are fairly rapid. The test compound may be decomposed in thirty minutes.

6.2.3 The TSD detector is capable of handling aqueous samples, however the removal of the analyte from the aqueous oxidant solution by extraction with ethyl acetate effectively stops the reaction and reduces problems with oxidants degrading column performance and chromatography in general.

6.2.4 The most effective use of resources in these kinetic studies requires timing of chromatography system startup and the chemical reaction being studied so that calibration samples are at the end of the run rather than at the beginning.

6.2.5 Deterioration of detector response to less than 75% of initial stable response may indicate the need to clean or replace the TSD ceramic bead.

6.3 Apparatus/Equipment

6.3.1 Analytical balance with 0.0001-gram sensitivity

6.3.2 120 ml amber bottles with Teflon-lined screw caps

6.3.3 Disposable glass pipettes

6.3.4 5 ml Plastic syringes and 0.45µm nylon filters

6.3.5 2 dram glass vials

6.3.6 Autosampler vials for Varian 8200 autosampler

6.3.7 A Varian 3400 gas chromatograph equipped with a Thermionic Specific Detector, a 1041 universal injector and a 15 meter DB5-MS 530u fused silica capillary column.

6.3.8 Vortex mixer

6.4 Reagents and Standards

6.4.1 Ethyl Acetate, EM Science Omni.Solv, glass distilled suitable for LC, GC used as a wash injection between samples.

6.4.2 O-ethyl-S-ethyl phenylphosphonothioate - synthesized at TVA, 98% pure.

6.4.3 Standards - Mix standards as outlined below. Store all standards in the refrigerator when not being used.

6.4.3.1 Primary standard - Add approximately 0.01g (weighed to the nearest 0.1 mg) of O-ethyl-S-ethyl phenylphosphonothioate to 100 ml ethyl acetate. (100 ppm)

6.4.3.2 Secondary standards - Dilute aliquots of the primary standard in ethyl acetate to make individual standards from 0.01 to 10 ppm before each run.

6.5 Quality Control Sample Requirements

6.5.1 Every tenth sample should be followed by a midpoint calibration standard run as a sample. Recovery should be 90 to 110% of the expected value.

6.5.2 With each batch of samples, run a laboratory control sample consisting of a sample with a concentration approximately equal to the midpoint of the calibration curve, but from the second primary standard stock. Recovery should be 90 to 110% of the expected value.

6.5.3 With each batch of samples, run a method blank through the extraction and analysis procedure.

6.5.4 Log and chart peak height of the initial midpoint calibration standard as an indicator of detector deterioration. See 6.2.5.

7.0 PROCEDURE

7.1 Calibration

7.1.1 Simultaneously with initiating the kinetic study under its planned experimental conditions, warm up the gas chromatograph.

7.1.2 Analyze a single 10 ppm standard at the start of the run. A complete set of standards is run following all experimental samples. The sample data are calculated from a linear regression fit of the standards utilizing chromatography workstation software.

7.1.3 A comparison is made of the peak height of the initial 10 ppm standard with that of previous runs to look for any major changes in response. See 6.2.5.

7.2 Procedure Instructions

7.2.1 Sampling and Extraction

7.2.1.1 According to the experimental design pull each sample at the appropriate time and immediately chill it by immersing it in ice water.

7.2.1.1 Utilizing information from the experimental design as to the total amount of O-ethyl-S-ethyl phenylphosphonothioate involved in the experiment, calculate the weight (or volume) of sample and volume of ethyl acetate needed to keep the concentrations within calibration range. Record weights and volumes in the research notebook.

Note: Small amounts of water are soluble in ethyl acetate. At 50:1 the water will be dissolved completely in the ethyl acetate phase so that the actual dilution becomes 51:1 in the final calculation. This is advantageous when extracting soil slurries because all water in the soil will be removed and extracted into the ethyl acetate phase.

7.2.1.3 Place the correct quantities of sample and ethyl acetate in a 2-dram vial.

7.2.1.4 Mix the sample and ethyl acetate on a vortex mixer for one minute.

7.2.1.5 Allow the extract to settle for approximately 5 minutes.

7.2.2 Place 1 ml of the ethyl acetate phase in an autosampler vial.

7.2.3 Load the samples into the autosampler and schedule the samples for analysis with the following operational parameters:

7.2.3.1 Gas Flow:
Carrier - Helium: 10 ml/minute
Makeup - Nitrogen 20 ml/minute
Auxiliary - Hydrogen 4.5 ml/minute
Air - 175 ml/minute

Pressure set at the regulator - Helium 80, Hydrogen 40, Air 60, Nitrogen 60

7.2.3.2 Temperature:

Injector: 200° C
Detector: 290° C
Oven: 100° C for 1.0 minute, then ramped at 20° C/minute to 240° C and held for 2.0 minutes.

Note: Run time including printout is 12 minutes.

7.2.3.3 Injection volume: 1 microliter (µL). Set in solvent flush mode with ethyl acetate at 1 µL as follows:

Autosampler type	8200
Special Sample Mode	User Defined Sample
Solvent Select	(ethyl acetate)
Solvent Flush Sampling	Yes
Syringe Wash Time	20 seconds
Solvent Plug Size	1.0
Vial Needle Depth	90%
Uptake Speed	5.0 ul/second
Upper Air Gap	Yes
Lower Air Gap	Yes
Pause Time	1 second
Hot Needle Time	0.00 minutes
Injection Rate	5.0 ul/second
Needle Residence Time	0.00 minutes

7.2.3.4 Retention time is 6.00 minutes plus or minus 0.05 minute.

7.3 Calculations and Recording Data

7.3.1 The calculations for the GC work are done by vendor-supplied software using the Varian Star Data Package.

7.3.2 Record all pertinent data such as sampling times, weights, volumes, peak areas, concentrations and reaction conditions in the research notebook.

7.3.3 Maintain copies of all workstation printouts.

7.3.4 Note any decisions to reject runs, decisions regarding peak identification, assessments of poor data, or the like on the workstation printouts or in the research notebook.

8.0 SAFETY

8.1 Handle all open samples containing O-ethyl-S-ethyl phenylphosphonothioate and perform all transfers of this material in a hood.

8.2 Routine laboratory protective clothing (lab coat, gloves, and eye protection) is all that is required for this procedure.

9.0 NOTES

9.1 Tested Concentration Range - The tested concentration ranges in water are: 0.01 to 10 mg/L

9.2 MDL for O-ethyl-S-ethyl phenylphosphonothioate is 0.0063 mg/L

9.3 Reporting Limit - 0.1 mg/L to 10 mg/L, $r^2 = 0.999$

9.4 Interferences - None noted

9.5 Analysis Rate - After instrument calibration , one analyst can analyze 25 samples in an 8 hour day (24-hour instrument day).

9.7 Chemical Abstact Service (CAS) numbers and selected physical properties of the analyte is:

Analyte	CAS#	b.p.
O-ethyl-S-ethyl phenylphosphonothioate	57557-80-9	89°C at 0.05 mm

10.0 ATTACHMENTS AND APPENDICES

None

End of Procedure

Appendix A-4 - Method AP-0050: Determination of peroxydisulfate, peroxymonosulfate, sulfate, and hydrogen peroxide in water by Raman Spectroscopy

Tennessee Valley Authority

Analytical Laboratory of Environmental Applications
Environmental Research Center
Muscle Shoals, AL 35662

Procedure Number : AP-0050

Title: Determination of Peroxydisulfate and Peroxymonosulfate in Water by Raman Spectroscopy

Signature	Title	Date
Prepared by: Paul D. Enlow	Research Chemist	3/4/97
Prepared by: William J. Rogers	Quality Assurance Officer	3/4/97
Concurred: James R. Pugh	Team Leader	3/4/97
Concurred:		
Approved: Joseph J. Hoagland	Manager	3/4/97

Revision	R0	R1				
Control Date	31-Jan-97	04-Mar-97				

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1.0 PURPOSE

This procedure describes actions required to measure peroxydisulfate and peroxymonosulfate by laser Raman spectroscopy for kinetic studies.

2.0 SCOPE

This method is applicable to determinations in water to measure relative concentration of the target compounds in kinetic studies.

3.0 SUMMARY

The liquid phase sample is placed in a cuvette and is illuminated by a laser at 514.5 nm. The light scattered by the sample is collectected at 90° to the incident laser beam. The Stokes Raman band is analyzed by a monochrometer, resulting in a Raman scattering spectrum. The concentration of the analyte is obtained by comparing its Raman peak intensity with a calibration curve.

4.0 REFERENCES

4.1 "User's Manual, Stabilite 2017 Ion Laser", Rev. B, February 1993, Spectra-Physics Lasers.

4.2 "Operation and Maintenance Instructions, 1403/1404 Spectrometer", Spex Industries, Inc.

4.3 "Spectramax Spectroscopic Acquisition and Analysis Software", Version 1.0, Instruments S. A.

5.0 RESPONSIBILITIES

5.1 It is the responsibility of the laboratory manager to ensure that this procedure is followed.

5.2 It is the responsibility of the team leader to review the results of the procedure.

5.3 It is the responsibility of the research chemist to follow this procedure, evaluate data, and to report any abnormal results or unusual occurrences to the team leader.

6.0 REQUIREMENTS

6.1 Prerequisites

6.1.1 Sampling times are determined prior to starting this procedure from an experimental design or plan.

6.1.2 Samples are taken and immediately chilled on ice to slow the reaction before delivery for analysis by this procedure.

6.2 Limitations and Actions

6.2.1 Reactions are fairly rapid. The test compound may be decomposed in thirty minutes under some test conditions.

6.3 Apparatus/Equipment

6.3.1 Analytical balance with 0.0001-gram sensitivity

6.3.2 1 cm x 1cm 0.7 mL volume quartz or glass cuvette (four sides polished).

6.3.3 Disposable glass pipettes

6.3.4 Plastic syringes, 5 mL.

6.3.5 Nylon filters, 0.45μm.

6.3.6 Assorted volumetric laboratory glassware.

6.3.7 Argon ion laser, Spectra-Physics 2017, 5 W combined line output, operated at 514.5 nm.

6.3.8 Double spectrometer, SPEX 1404, 0.85 m focal length, equipped with 1800 lines/mm holographic gratings and a Hamamatsu R928P photomultiplier tube. The resolution for this grating at 514.5 nm is 0.0027 nm (0.10 cm^{-1}).

6.3.9 Power meter, Spectra-Physics 407A.

6.3.10 Fiber optic collection system, SPEX 1700F, fitted with an Oriel 77662 focusing beam probe.

6.3.11 Best-form laser lens, 100 mm focal length.

6.3.12 Lyot-wedge depolarizer.

6.4 Reagents and Standards

6.4.1. Potassium persulfate, 99+%, Aldrich

6.4.2 Oxone peroxymonosulfate compound, Aldrich

6.4.3 Deionized water.

6.4.4 Standards - Store standards in the refrigerator (approximately 4°C) when not being used

6.4.4.1 Peroxydisulfate primary standard - Weigh approximately 4 g of potassium persulfate to an accuracy of 0.1 mg. Add water to make 100 ml of total solution. Calculate the molarity of the peroxydisulfate ion in this solution. A seven point calibration curve will be made with dilutions of this stock solution. (See Notes 9.8 and 9.9).

6.4.4.2 Peroxymonosulfate primary standard - Weigh approximately 4 g of Oxone to an accuracy of 0.1 mg. Add water to make 100 ml of total solution. Calculate the molarity of the peroxymonosulfate ion in this solution. Note that one mole of Oxone contains two moles of the peroxymonosulfate ion. A six point calibration curve will be made with dilutions of this stock solution. (See Notes 9.8 and 9.9).

6.4.4.3 Midpoint calibration standard (peroxydisulfate) - Weigh approximately 2 g of potassium persulfate to an accuracy of 0.1 mg. Add water to make 100 ml of total solution. Calculate the molarity of the peroxydisulfate ion in this solution.

6.4.4.4 Midpoint calibration standard (peroxymonosulfate) - Weigh approximately 2 g of Oxone to an accuracy of 0.1 mg. Add water to make 100 ml of total solution. Calculate the molarity of the peroxymonosulfate ion in this solution. Note that one mole of Oxone contains two moles of the peroxymonosulfate ion.

6.4.4.5 Calibration standards - dilute suitable volumes of the primary standard with water to make individual standards of 4, 2, 1, 0.2, 0.1, 0.05, and 0.025 g/L for the peroxydisulfate, and 4, 2, 1, 0.2, 0.1, and 0.05 g/L for the peroxymonosulfate.

Note: The calibration curve for the peroxydisulfate contains an additional point because it has a lower detection limit than the peroxymonosulfate.

6.5 Quality Control Sample Requirements

6.5.1 With each batch of samples, run a midpoint calibration standard. Recovery should be 85 to 115% of the expected value.

6.5.2 If the recovery in step 6.4.1 falls outside the range of 85 to115 %, make a new set of calibration standards and run a new calibration curve.

7.0 PROCEDURE

7.1 Laser start up and shutdown

7.1.1 Start up

7.1.1.1 Turn on the laser operation light in the hallway outside the laboratory.

7.1.1.2 Turn on the cooling water.

7.1.1.3 Turn on power to the laser power supply.

7.1.1.4 Verify that the laser is in constant current mode, not constant power mode.

7.1.1.5 Insert the key into the power supply remote control box and turn it on. Set the amperage at 10 A. No lasing is possible below 10A. The laser will begin lasing after a several second delay If no laser line is evident, the horizontal and/or vertical mirrors may need adjustment; refer to the laser user's manual.

7.1.1.6 Bring the laser up to the desired power level by increasing the amperage at a rate no greater than 5 A every 5 minutes. The power level for sample analysis is 1150 mW. The power level for alignment of cuvettes and optical elements is approximately 10 mW. A neutral density filter may be used to lower the power for alignment.

7.1.1.7 Set the laser on constant power mode if samples are to be run.

7.1.2 Shutdown

7.1.2.1 After all measurements are complete, shut down the laser by decreasing the amperage at a rate no greater than 5 A every 5 minutes until the current reads 10 A. Hold at 10 A for 5 minutes.

7.1.2.2 Turn off the key and remove it from the power supply remote control box. Turn off the power to the power supply. Turn off the laser operation light in the hallway.

7.1.2.3 Cut off the cooling water after 5 minutes.

7.2 Equipment set-up

This section is necessary only if samples are to be run for the first time or if the cell holder or collection optics have been changed or moved.

7.2.1 Turn on the laser according to section 7.1.1 and adjust the output to approximately 100 mW.

7.2.2 Put the depolarizer in the beam path.

7.2.3 Place the cell holder in the beam path about 20 mm from the focusing beam probe (FBP). An imaginary line drawn from the lens of the FBP to the center of the cell holder must be perpendicular to the laser beam.

7.2.4 Fill the cell with the potassium peroxydisulfate primary standard and place it in the cell holder.

7.2.5 Place the laser focusing lens in the beam path 100 mm from the center of the cell.

7.2.6 Verify that the focused laser beam is passing through the 2 mm wide window of the cell.

7.2.7 Set the spectrometer to 1082 cm^{-1} and begin collecting a real-time spectrum.

7.2.8 Adjust the cell holder position along the beam path until the collected signal is at a maximum.

7.2.9 Adjust the FBP distance from the cell holder until the collected signal is at a maximum.

7.2.10 Adjust the position of the two collimating lenses inside the fiber optic collection system until the collected signal is at a maximum.

7.2.11 Verify that all positions and distances in steps 7.2.8 through 7.2.10 are optimized by changing them slightly, one at a time. The signal should decrease in each case. If it does, then return the item to its original position. If the signal does not decrease, then adjust that item until the signal is at a maximum.

7.2.12 Repeat step 7.2.11 until the signal cannot be made to increase.

7.2.13 Lock all components in position.

7.3 Calibration

7.3.1 Calibration curve

7.3.1.1 Adjust the laser power to 1150 mW according to section 7.1.1.

7.3.1.2 Place a calibration standard from step 6.4.4.5 into the cuvette.

7.3.1.3 Place the cuvette in the cell holder.

7.3.1.4 Record a Raman spectrum of the standard using the following parameters:
Resolution = 2 cm
Number of scans averaged = 10
Photomultiplier voltage = 950 V
Integration time = 0.4 seconds
Wavelength range(s):
For peroxydisulfate: 1050 to 1100 cm^{-1}
For peroxymonosulfate: 850 to 910, and 1040 to 1100 cm^{-1}

Note: For the lowest concentrations, the signal/noise ratio will be increased by a factor of 7 by increasing the number of scans averaged to 49. This will make it easier to measure the peak heights.

7.3.1.5 Repeat steps 7.3.1.2 to 7.3.1.4 for all standards.

7.3.1.6 Calculate calibration curve fit according to section 7.5.

7.3.2 Midpoint calibration check

7.3.2.1 Run a mid-point calibration standard with each batch of samples.

7.3.2.2 Record a Raman spectrum of a calibration standard from 6.3.4.3 or 6.3.4.4 according to section 7.3.1. Recovery as calculated in section 7.5 should be 85 to 115% of the expected value.

7.4 Procedure Instructions

7.4.1 Adjust the laser power to 1150 mW according to section 7.1.1, and verify that the laser is in constant power mode.

7.4.2 If the sample looks turbid, filter it through a 0.45µ syringe filter.

7.4.3 Rinse the cuvette three times with a portion of the sample to be measured. Place the sample into the cuvette.

7.4.4 Place the cuvette into the cell holder

7.4.5 Measure the laser output with the power meter, and adjust it to 1150 mW if necessary.

7.4.6 Record a Raman spectrum of the sample using the following parameters:
Resolution = 2 cm
Number of scans averaged = 10
Photomultiplier voltage = 950 V
Integration time = 0.4 seconds
Wavelength range(s):
For peroxydisulfate: 950 to 1100 cm^{-1}
For peroxymonosulfate: 850 to 1100cm^{-1}

Note: For the lowest concentrations, the signal/noise ratio will be increased by a factor of 7 by increasing the number of scans averaged to 49. This will make it easier to measure the peak heights. If this makes the analysis times too long, the wavelength ranges may be changed to 1050 to 1100 cm^{-1} for the peroxydisulfate, and to 850 to 910 cm^{-1}, and 1040 to 1100 cm^{-1} for the peroxymonosulfate.

7.4.7 Rinse the cuvette with deionized water.

7.4.8 Calculate the sample concentration according to section 7.5.

7.5 Calculations and Recording Data

7.5.1 Peak height measurement - determine the difference in counts between the peak maximum and the average of the baseline values on either side of the peak. Record the file name, peak maximum, baseline values on either side of the peak, peak height calculated, and wavenumbers at which baseline values were determined.

7.5.2 Calibration curve

7.5.2.1 Plot a graph of the peak height of the standards vs. Concentration in mM.

7.5.2.2 Calculate a liner regression curve fit for the points plotted in 7.5.2.1, and express the resulting line in the form $Y = mX + b$, where:
m = the slope of the line
b = the Y intercept
Y = The peak height in counts
X = Concentration in mM

7.5.3 Concentration of midpoint calibration standards and samples:

$X = (Y-b)/m$

All symbols are the same as in 7.5.2.2.

8.0 SAFETY

8.1 Handle all open samples and perform all transfers in a hood.

8.2 Routine laboratory protective clothing (lab coat, gloves, and eye protection) is required for this procedure when handling samples.

8.3 Wear laser goggles while aligning sample cell when the laser is on.

9.0 NOTES

9.1 The tested concentration range is 0.5 to 37 g/L

9.2 Detection Limits

Analyte	MDL
Potassium peroxydisulfate	0.12 g/L
Oxone	0.57 g/L

9.3 Reporting Limits

0.5 g/L to 37 g/L $r^2 = 0.999$

9.4 Interferences - Soil particles and other suspended matter will cause the incident laser beam to scatter. These interferences are removed by filtering the sample prior to analysis.

9.5 Analysis rate - 3 samples/hour (10 scans)

9.6 Vendors for standards - Aldrich

9.7 Chemical Abstract Service numbers and selected physical properties of the analytes and their decomposition products are:

Analyte Name	CAS#	O-O stretching frequency (cm^{-1})	S=O stretching frequency (cm^{-1})
Potassium Peroxydisulfate	7727-21-1	840	1078
Potassium Peroxymonosulfate (from Oxone)	37222-66-5	884	1062
Potassium Sulfate	7778-80-5	none	984
Hydrogen Peroxide	7722-84-1	880	none

9.8 Calculation of molarity in steps 6.4.4.1 and 6.4.4.2.

The concentration of the standards is given by

$$mM = (1000)AW/VF$$

Where:
mM = concentration of the standard in millimolar (millimoles per liter)
A = molar ratio.
A = 1 for potassium peroxydisulfate
A = 2 for potassium peroxymonosulfate
W = weight of standard used
V = volume of solution in liters
F = formula weight of salt used.
F = 270.33 for potassium peroxydisulfate
F = 614.78 for potassium peroxymonosulfate (Oxone)

9.9 Conversion of molarity to mg/L

$$C = (mM)F$$

Where:
C = concentration in mg/L
mM = concentration of analyte in millimolar
F = formula weight of analyte.
F = 192.13 for the peroxydisulfate ion
F = 113.07 for the peroxymonosulfate ion

10.0 ATTACHMENTS AND APPENDICES

None

End of Procedure

Appendix A-5 - Method AP-0051: Determination of Chloroethyl ethylsulfide chloroethyl phenylsulfide, and their degradation products by high performance liquid chromatography.

Tennessee Valley Authority

Analytical Laboratory of Environmental Applications
Environmental Research Center
Muscle Shoals, AL 35662

Procedure Number : AP-0051

Title: Determination of Chloroethyl Ethylsulfide,Chloroethyl Phenylsulfide, and Their Degradation Products by High Performance Liquid Chromatography

Signature	Title	Date
Prepared by: James A. Farley James A. Farley	Research Chemist	3/3/97
Prepared by: William J. Rogers William J. Rogers	Quality Assurance Officer	3/3/97
Concurred: James R. Pugh James R. Pugh	Team Leader	3/3/97
Concurred:		
Approved: Joseph J. Hoagland	Manager	3/3/97

Revision	R0	R1				
Control Date	31-Jan-97	03-Mar-97				

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Determination of Chloroethyl Ethylsulfide,Chloroethyl Phenylsulfide, and Their Degradation Products by High Performance Liquid Chromatography

1.0 PURPOSE

This procedure describes actions required to measure chloroethyl ethylsulfide (CEES), chloroethyl phenylsulfide (CEPSI), and their degradation products by high performance liquid chromatography for kinetic studies.

The degradation products are: thiodiglycol (TDG), hydroxyethyl ethylsulfide (HEES), hydroxyethyl phenylsulfide (HEPSI), chloroethyl phenylsulfone (CEPSO), chloroethyl phenylsulfoxide (CEPSX), hydroxyethyl phenylsulfone (HEPSO), oxathiane (1,4-T), 1,4-dithiane (1,4-D), vinylsulfone (VSO), phenyl vinylsulfone (PVSO)

2.0 SCOPE

This method is applicable to determinations in aqueous solutions and soil slurries to measure relative concentration of all but two of the target compounds (CEES and CEPSI) for kinetic studies. The method is applicable to determination of CEES and CEPSI in organic solvents.

3.0 SUMMARY

In a kinetic study, a series of samples is taken as a function of time under various reaction conditions. For each sample, the reaction is first quenched by chilling. Aqueous samples and soil slurry samples are filtered then directly injected and analyzed by HPLC. Organic extracts are filtered and directly injected and analyzed by HPLC. CEPSI is determined under separate operating conditions from the other analytes.

4.0 REFERENCES

4.1 "Detection of Thiodiglycol and its Sulfoxide and Sulfone Analogues in Environmental Waters by High Performance Liquid Chromatography," Edgewood Research, Development, and Engineering Center, ERDEC-TR-035, Paul C. Bossie, Machael W. Ellzy, and John J. Martin, June 1993, Aberdeen Proving Ground, Maryland 21010-5423.

4.2 "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods", SW-846, 3rd Edition, Most Recent Update (July 1992 with proposed methods dated November 1992)

Chapter 1, "Quality Assurance"

Chapter 4, "Organic Analysis"

Method 8000A, "Gas Chromatography", Chapter 8.

Method 8330A, "Nitroaromatics and Nitramines by High Performance Liquid Chromatography (HPLC)"

5.0 RESPONSIBILITIES

5.1 It is the responsibility of the laboratory manager to ensure that this procedure is followed.

5.2 It is the responsibility of the team leader to review the results of the procedure.

5.3 It is the responsibility of the laboratory analyst to follow this procedure and to report any abnormal results or unusual occurrences to the laboratory group leader.

6.0 REQUIREMENTS

6.1 Prerequisites

6.1.1 Sampling times are determined prior to starting this procedure from an experimental design or plan. Sampling times and pertinent experimental data are recorded in a research notebook.

6.1.2 Samples are chilled prior to delivery for analysis to quench the reaction.

6.2 Limitations and Actions

6.2.1 Quenching of the reaction by chilling should be done as soon as possible after sampling. Analysis should follow as rapidly as possible.

6.2.2 Two compounds, CEES and CEPSI, hydrolyze in water to form HEES and HEPSI, respectively. CEES and CEPSI can only be analyzed from an organic solvent.

6.3 Apparatus/Equipment

6.3.1 Analytical balance with 0.0001-gram sensitivity

6.3.2 120 ml amber bottles with Teflon-lined screw caps

6.3.3 Disposable glass pipettes

6.3.4 5 ml Plastic syringes and 0.45µm nylon filters

6.3.5 2 dram glass vials

6.3.6 0.5 ml glass syringe

6.3.7 Magnetic stirrers/heaters and stir bars

6.3.8 High Performance Liquid Chromatography System - Dionex GPM-2 gradient pump, Hewlett Packard Series 1050 MWD detector, Valco 6 port injector, Supelco column (150 x 4.6 mm Supelcosil C18 ODS) and a Hewlett Packard 3390A integrator.

6.3.9 Ultrasonic bath

6.4 Reagents and Standards

6.4.1. Acetonitrile, EM Science Omni.Solv glass distilled suitable for LC, GC

6.4.2 Acetone, EM Science OmniSolv, suitable for LC, GC

6.4.3 Deionized water.

6.4.4 Standards - Store standards in the refrigerator (approximately 4°C) when not being used

6.4.4.1 Primary standard - dilute approximately 0.050g (weight recorded to the nearest 0.1mg) of each compound to 50ml with the solvent listed in note 9.1. Adjust the calculated concentration for purity. Prepare fresh standards every 60 days.

6.4.4.2 Calibration standards - dilute suitable volumes of each primary standard with the solvent listed in note 9.1 to make five individual (CEES or CEPSI) or five mixed standards that are in the concentration ranges given in note 9.1. Prepare new calibration curves every 60 days.

6.5 Quality Control Sample Requirements

6.5.1 Begin each run by measuring a midpoint calibration standard run as a sample. When the run is long enough, every tenth sample should be followed by a midpoint calibration standard run as a sample. Recovery should be 90 to 110% of the expected value.

6.5.2 With each batch, run a reagent blank.

7.0 PROCEDURE

7.1 Calibration

7.1.1 Analyze the five mixed (or individual for CEES or CEPSI) standards. Calculate a linear regression fit through the data utilizing a commercial curve-fitting software package or spreadsheet. Record the concentrations, peak areas, fit parameters, and r^2 values for each curve in the laboratory notebook.

7.1.2 Before samples are analyzed in each run, a midpoint standard is analyzed to check calibration. A comparison is made with previous runs to look for any major changes in response.

7.2 Procedure Instructions

7.2.1 Extraction and Filtration

7.2.1.1 According to the experimental plan, pull each sample at the appropriate time and immediately chill it by immersing it in ice water.

7.2.1.2 For water and soil slurry samples, filter the aqueous phase through a syringe filter.

7.2.1.3 For dry soil samples for CEES or CEPSI analysis, place two grams of sample in 100 ml acetonitrile in an ultrasonic bath for 10 minutes.

7.2.1.4 Filter the acetonitrile phase through a syringe filter.

7.2.2 Analytical Parameters

7.2.2.1 For all analytes but CEPSI, inject the samples with the following operational parameters:

Mobile phase: 50% methanol/ 50% water (isocratic)
Detector: 210 nm
Injection volume: 20 µL
Multiplication factor: 2.0
Run time: 20 minutes
Flow rate: 1 mL/minute
Temperature: ambient

7.2.2.2 For CEPSI, inject the samples with the following operational parameters:

Mobile phase: 80% methanol/ 20% water.
Detector: 210 nm
Injection volume: 20 µL
Multiplication factor: 2.0
Run time: 20 minutes
Flow rate: 1 mL/minute
Temperature: ambient

7.2.3 Typical retention times in minutes:

CEES	13.90
HEES	3.12
TDG	2.13
CEPSI	4.54
HEPSI	7.03
HEPSO	2.53
CEPSO	4.56
CEPSX	17.49
VSO	2.27
PVSO	3.57
1,4-D	6.88
1,4-T	3.40

7.3 Calculations and Recording Data

7.3.1 Determine the peak area for the analyte of interest utilizing chromatography workstation software.

7.3.2 Using the linear regression equation determined during calibration, calculate sample concentration.

7.3.3 Record all pertinent data such as sampling times, weights, volumes, peak areas, concentrations and reaction conditions in the research notebook.

7.3.4 Maintain copies of all workstation printouts.

7.3.5 Note any decisions to reject runs, decisions regarding peak identification, assessments of poor data, or the like on the workstation printouts or in the research notebook.

8.0 SAFETY

8.1 Handle all open samples and perform all transfers in a hood.

8.2 Routine laboratory protective clothing (lab coat, gloves, and eye protection) is all that is required for this procedure .

9.0 NOTES

9.1 The tested concentration ranges are:

Analyte	Range (mg/L)	Solvent
CEES	3.8 to 189	$(CH_3)_2O$
HEES	1.2 to 118	H_2O
TDG	3.4 to 168	H_2O
VSO	0.9 to 88	H_2O
1,4-T	1.0 to 105	H_2O
1,4-D	1.3 to 132	H_2O
CEPSI	0.50 to 125	CH_3CN
CEPSO	0.50 to 37	H_2O
CEPSX	0.73 to 62	H_2O
PVSO	0.12 to 23	H_2O
HEPSI	0.34 to 60	H_2O
HEPSO	0.35 to 70	H_2O

9.2 Detection Limits

Analyte	MDL mg/L
CEES	0.82
HEES	0.09
TDG	0.12
VSO	0.04
1,4-T	0.04
1,4-D	0.02
CEPSI	0.09
CEPSO	0.02
CEPSX	0.17
PVSO	0.01
HEPSI	0.01
HEPSO	0.01

9.3 Reporting Limits

Analyte	Range (mg/L)	r^2
CEES	3.8 to 189	0.9999
HEES	1.2 to 118	0.9999
TDG	3.4 to 168	0.9983
VSO	0.9 to 88	0.9990
1,4-T	1.0 to 105	0.9999
1,4-D	1.3 to 132	0.9999
CEPSI	0.50 to 125	0.9998
CEPSO	0.50 to 37	0.9972
CEPSX	0.73 to 62	0.9998
PVSO	0.12 to 23	0.9969
HEPSI	0.34 to 60	0.9999
HEPSO	0.35 to 70	0.9997

9.4 Interferences - None noted.

9.5 Recovery - Extractions from soils gave

Analyte	% Recovery	Solvent
CEES	103.0	Acetonitrile
HEES	99.1	Water
TDG	100.5	Water
CEPSI	96.0	Acetonitrile
HEPSI	89.9	Water
HEPSO	94.9	Water
CEPSO	97.3	Water
CEPSX	86.8	Water
PVSO	89.7	Water
VSO	98.9	Water
1,4-D	95.4	Water
1,4-T	96.9	Water

9.6 Analysis rate - 20 minute run time

9.7 Vendors for standards - Aldrich

Analyte code	Lot Number	Purity
CEES	15505LN	98 %
HEES	02008CL	97 %
TDG	16717JN	99 %
CEPSI	11628MG	98 %
HEPSI	12820MG	99 %
HEPSO	02326JF	97 %
CEPSO	14827DN	98 %
CEPSX	05421MZ	99 %
1,4-T	03808JF	98 %
1,4-D	03630JP	97 %
VSO	04706AG	97 %
PVSO	24018EF	99 %

9.8 Selected physical properties for the analytes are:

Analyte Code	CAS #	m.p., °C	b.p., °C	density, g/mL
CEES	693-07-2		156	1.070
HEES	110-77-0		182	1.020
TDG	111-48-8	-16	165	1.221
CEPSI	5535-49-9	90		1.174
HEPSI	699-12-7		116	1.143
HEPSO	20611-21-6		177	1.557
CEPSO	938-09-0	56	170	
CEPSX	13457-98-2		132	1.070
PVSO	5535-48-8	68		
VSO	77-77-0	-26	234	1.177
1,4-D	505-29-3	111	200	
1,4-T	15980-15-1		147	1.114

10.0 ATTACHMENTS AND APPENDICES

None

End of Procedure

Appendix A-6 - Method AP-0053: Determination of methylphosphonic acid, O-ethyl phenylphosphonic acid, phenylphosphonic acid, ethanesulfonic acid, and phosphate in water by ion chromatography.

Tennessee Valley Authority

Analytical Laboratory of Environmental Applications
Environmental Research Center
Muscle Shoals, AL 35662

Procedure Number : AP-0053

Title: Determination of Methylphosphonic Acid, O-ethyl Phenylphosphonic Acid, Phenylphosphonic Acid, Ethanesulfonic Acid, and Phosphate in Water by Ion Chromatography

Signature	Title	Date
Prepared by: James A. Farley	Research Chemist	3/20/97
Prepared by: William J. Rogers	Quality Assurance Officer	3/20/97
Concurred: James R. Pugh	Team Leader	3/20/97
Concurred:		
Approved: Joseph J. Hoagland	Manager	3/20/97

Revision	R0	R1	R2			
Control Date	31-Jan-97	03-Mar-97	24-Mar-97			

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Determination of Methylphosphonic Acid, O-ethyl phenylphosphonic acid, Phenylphosphonic Acid, Ethanesulfonic Acid, and Phosphate in Water by Ion Chromatography

1.0 PURPOSE

This procedure describes actions required to measure methylphosphonic acid (MPA), O-ethyl phenylphosphonic acid (OEPPA), phenyl phosphonic acid (PPA), ethanesulfonic acid (ESA), and phosphate (PO_4^{-3}) by ion chromatography for kinetic studies.

2.0 SCOPE

This method is applicable to determinations in water and soil slurries to measure relative concentration of the target compounds in kinetic studies.

3.0 SUMMARY

The sample is filtered, run through a barium column to remove sulfate, and analyzed with an ion chromatograph.

4.0 REFERENCES

4.1 "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods", SW-846, 3rd Edition, Most Recent Update (July 1992 with proposed methods dated November 1992), Chapter 1, "Quality Assurance"

4.2 "Determination of Anions by Ion Chromatography," Section 4110, Standard Methods for the Examination of Water and Wastewater, 19th Edition, 1995, Edited by Andrew D. Eaton, Lenore S. Clesceri, and Arnold E. Greenburg

5.0 RESPONSIBILITIES

5.1 It is the responsibility of the laboratory manager to ensure that this procedure is followed.

5.2 It is the responsibility of the team leader to review the results of the procedure.

5.3 It is the responsibility of the laboratory analyst to follow this procedure and to report any abnormal results or unusual occurrences to the laboratory group leader.

6.0 REQUIREMENTS

6.1 Prerequisites

6.1.1 Sampling times are determined prior to starting this procedure from an experimental design or plan. Sampling times and pertinent experimental data are recorded in a research notebook.

6.2 Limitations and Actions

6.2.1 Quenching of the reaction by chilling should be done as soon as possible after sampling. Further preparation should follow as rapidly as possible.

6.2.2 Reactions are fairly rapid. Measurements should be made as rapidly as possible.

6.2.3 Perform calibrations every 60 days or when quality control samples indicate recalibration is needed.

6.3 Apparatus/Equipment

6.3.1 Analytical balance with 0.0001-gram sensitivity

6.3.2 120 ml amber bottles with Teflon-lined screw caps

6.3.3 Disposable glass pipette

6.3.4 5 ml Plastic syringes and 0.45µm nylon filters

6.3.5 2 dram glass vials

6.3.6 0.5 ml glass syringe

6.3.7 Magnetic stirrers/heaters and stir bars

6.3.8 Dionex ion chromatography system - 2120 Automated IC module, advanced IC module, analytical pump, conductivity detector, and autoion chromatography software. An Ionpac AS4A column, AG4A guard column, and AMMS-1 autoion suppresser column will be used to separate the analytes.

6.4 Reagents and Standards

6.4.1. Maxi-clean IC-Ba cartridges, Alltech

6.4.2 Acetone, EM Science OmniSolv, suitable for high resolution GC

6.4.3 Deionized water.

6.4.4 Standards - Store standards in the refrigerator (approximately 4°C) when not being used.

6.4.4.1 Primary standard - dilute approximately 0.050g (weight recorded to the nearest 0.1mg) of each compound to 50 ml with deionized water. Adjust the calculated concentration for purity. Prepare fresh standards every 60 days.

6.4.4.2 Calibration standards - dilute suitable volumes of each primary standard with deionized water to make individual or mixed standards that are in the concentration range given in note (9.1). Prepare new calibration curves every 60 days.

6.5 Quality Control Sample Requirements

6.5.1 Begin each run by measuring a midpoint calibration standard run as a sample. Recovery should be 90 to 110% of the expected value.

6.5.2 Every tenth sample should be followed by a midpoint calibration standard run as a sample. Recovery should be 90 to 110% of the expected value.

6.5.2 With each batch, run a reagent blank.

6.5.3 Log and chart peak height of the initial midpoint calibration standard as an indicator of column performance. See 6.5.2

7.0 PROCEDURE

7.1 Calibration

7.1.1 Analyze the mixed standards. Calculate a linear regression fit through the data utilizing a commercial curve-fitting software package or spreadsheet. Record the concentrations, peak areas, fit parameters, and r^2 values for each curve in the laboratory notebook.

7.1.2 Before samples are analyzed in each run, a mixed standard is analyzed to check calibration. A comparison is made with previous runs to look for any major changes in response.

7.2 Procedure Instructions

7.2.1 Sample Preparation

7.2.1.1 Place the sample in a syringe barrel fitted with a barium column and filter.

7.2.1.2 Fit the plunger in the barrel and pass the sample through the barium column and filter at a rate of about 1 ml/minute.

7.2.1.3 If the sample is cloudy, pass it through another barium column and filter.

7.2.2 Load the samples for analysis with the following operational parameters:

Eluent: 1.8 mM Na_2CO_3/1.7 mM $NaHCO_3$
Flow rate: 2.0 mL/min or 1.0 mL/min (see note 9.2)
Regenerant: 50 mN H_2SO_4
Sample loop volume: 50µL
Run time: 20 minutes
Temperature: Ambient

7.2.3 Typical retention times in minutes:

Analyte name	retention time
MPA	3.63 min
PPA	6.45 min
ESA	1.25 min
PO_4^{-3}	4.75 min
OEPPA	1.40 min

7.3 Calculations and Recording Data

7.3.1 Determine the peak area for the analyte of interest utilizing chromatography workstation software.

7.3.2 Using the linear regression equation determined during calibration, calculate sample concentration.

7.3.3 Record all pertinent data such as sampling times, weights, volumes, peak areas, concentrations and reaction conditions in the research notebook.

7.3.4 Maintain copies of all workstation printouts.

7.3.5 Note any decisions to reject runs, decisions regarding peak identification, assessments of poor data, or the like on the workstation printouts or in the research notebook.

8.0 SAFETY

8.1 Handle all open samples and perform all transfers in a hood.

8.2 Routine laboratory protective clothing (lab coat, gloves, and eye protection) is all that is required for this procedure .

9.0 NOTES

9.1 The tested concentration ranges are:

Analyte	Range	Solvent
MPA	0.68 to 171 mg/L	Water
PPA	1.2 to 120 mg/L	Water
ESA as ethanesulfonic acid, sodium salt	0.80 to 80 mg/L	Water
PO_4^{-3} as potassium hydrogen phosphate	0.60 to 149 mg/L	Water
OEPPA	1.3 to 134 mg/L	Water

9.2 For experiments involving degradation of diisopropyl methylphosphonate (DIMP), only MPA and PO_4^{-3} are observed. A flow rate of 2.0 ml/minute is used. For experiments involving degradation of O-ethyl-S-ethyl phenylphosphonothioate, the simulant for VX; PPA, ESA, OEPPA, and PO_4^{-3} are observed. A flow rate of 1 ml/minute must be used so that ESA may be resolved from OEPPA. With this flow rate, the following retention times are observed.

Analyte name	CAS #	retention time
PPA	1571-33-1	12.90 min
ESA	5324-47-0	2.50min
PO_4^{-3}		9.40 min
OEPPA		2.80 min

9.3 Detection Limits

Analyte	MDL
MPA	0.20 mg/L
PPA	0.34 mg/L
ESA	0.29 mg/L
PO_4^{-3}	0.20 mg/L
OEPPA	0.78 mg/L

9.4 Reporting Limits

Analyte	Range	r^2
MPA	0.68 to 171 mg/L	0.9994
PPA	1.2 to 120 mg/L	0.9976
ESA	0.80 to 80mg/L	0.9994
PO_4^{-3}	0.60 to 149 mg/L	0.9992
OEPPA	1.3 to 134 mg/L	0.9996

9.5 Interferences -Due to the very large concentrations of sulfate present in concentrated Oxone solutions or aged peroxydisulfate solutions, changes in retention times may occur. To overcome the sulfate interferences, the sulfate is removed as $BaSO_4$ by passing each sample through an Alltech Maxi-clean IC-Ba cartridge prior to injection.

9.6 Recovery Data from Soil

Analyte	% Recovery
MPA	101.1
PPA	96.4
ESA	101.3
PO_4^{-3}	96.5
OEPPA	97.7

9.7 Analysis rate - 20 minute run time

10.0 ATTACHMENTS AND APPENDICES

None

End of Procedure